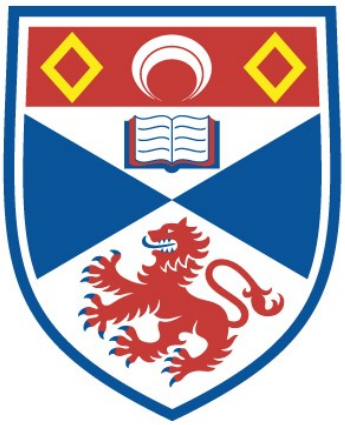
OPTICAL PROPERTIES OF METALS AT LOW TEMPERATURES

David C. Baird

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE OPTICAL PROPERTIES OF METALS AT LOW TEMPERATURES

being a thesis presented by

David C. Baird, B.Sc.

to the University of St. Andrews

in application for the degree of Doctor of Philosophy.

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DECLARATION

I hereby declare that the following thesis is based on the results of experiments carried out by me, that the thesis is my own composition and that it has not been previously presented for a higher degree in this or any other University. The research was carried out in the Physical Laboratory of the United College of the University of St. Andrews under the direction of Professor J.F. Allen, F.R.S.

CERTIFICATE

I certify that David C. Baird, B.Sc., has spent nine terms at research work in the Physical Laboratory of the United College of the University of St. Andrews under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the Degree of Doctor of Philosophy.

CAREER

I matriculated in the University of Edinburgh in October 1945 and followed the course leading to graduation with the degree of Bachelor of Science. In October 1949 I commenced research in the Natural Philosophy Department, United College, St. Andrews University on the work which is now presented as a thesis for the degree of Doctor of Philosophy.

SUMMARY

The work to be described deals with the reflectivity of metals at temperatures down to 20° K. A historical introduction shows how the development of electronic optical theory led to an understanding of many of the important optical properties of metals while leaving unexplained an anomalously high absorbing power. The Maxwellian phenomenological and the electronic theories are given and their limitations noted. The method chosen for the measurement of reflectivity uses a double beam system with continuous balancing and the main features of the apparatus are described. The mirror surfaces have been prepared by electrolytic polishing, by casting and by annealing. The experimental procedure is described in detail and a discussion of the sources of error is given.

The variation of reflectivity with both temperature and wavelength has been measured but no absolute measurements of reflectivity were made. The d.c. resistivity of comparable samples was measured over most of the above temperature range. The reflectivity results show features which are identified with the behaviour expected as a result of a theory due to Reuter and Sondheimer. On this basis it is concluded that present theories are still inadequate to account for all the optical absorption found in metals.

CONTENTS

CHAPTER I

The property possessed by metals of conducting electricity was first taken into account in electromagnetic theory in a purely empirical manner. In the development of the equations derived by Maxwell, the assumption is made that a simple relation $\underline{J} = \sigma \underline{E}$ exists between the electric field applied at a point in a conducting medium and the resulting current at that point, thus defining a conductivity σ. So long as this assumption was made the treatment was obliged to remain phenomenological and no progress towards the understanding of the conduction processes could be made. The recognition by J. J. Thomson of the electron as a fundamental particle made possible the proposal of mechanisms for the conductivity of metals and the properties of various models were worked out by Drude, Lorentz and others.

In these early classical theories, the metal was assumed to be a solid which differed from an insulator in that it contained a number of electrons which were detached from the atoms of the solid and were free to move from point to point in the material. These electrons were considered to have the properties of a perfect gas and the phenomena of conduction were treated by the already standard methods of gas kinetics. The electrons were assumed to have a velocity depending on the temperature of the metal and their progress to be limited by collision processes to a mean free path. The result of this is that, in the presence of an electric field, the electron will have, superimposed on its random velocity, an acceleration in the direction of the field. If it is assumed that all the drift velocity is lost at each collision, this simple model leads to very reasonable expressions for the electrical and thermal conductivities of metals. Certainly, difficulties are encountered in explaining low temperature

conductivities where the low velocities of the electrons required by the assumed temperature variation necessitate the assumption of excessively long free paths but the treatment is successful in the prediction of the Wiedemann-Franz law connecting the thermal and electrical conductivities, although the value of the Lorenz number is wrong. These theories also give plausible explanations for other metallic properties such as thermo-electricity, thermionic emission and optical behaviour. The characteristic features of metallic reflection are assumed to be the result of the fact that an electron, oscillating under the influence of an alternating radiation field will re-emit radiation of the same frequency as the incident beam, leading to a reflecting power high compared with that of insulators. The properties of such a system of electronic oscillators were calculated by Drude (1904) obtaining formulae for the optical constants and reflectivity of the metal.

This came at an opportune time to check with the work of Paschen (1901) and Hagen and Rubens (1902) who had been measuring the reflecting power of a number of metals at wave-lengths ranging from the ultra-violet to the infra-red. They had been considering their results in terms of formulae derived directly from the Maxwell equations. The optical properties could be considered without requiring a detailed model for conduction and general expressions for the optical constants of metals can be obtained using the Maxwell treatment. The formulae obtained can be considerably simplified by making the assumption of good conductivity and low frequency of incident radiation and lead to the conclusion that the absorbing power for any particular wave-length ought, at least for wave-lengths of about 1 μ and greater, to be proportional to the square root of the resistivity of the metal. However, Hagen and Rubens had come

to the conclusion that, even although the theory does assume infra-red wave-lengths, much longer wave-lengths yet were necessary to give agreement between experiment and theory. The new electron gas theory now made it clear that a discrepancy was to be expected on account of the mass of the electrons which must limit their response to alternating electric fields. This inertial effect would produce in the d.c. conductivity only a transient term which would not be observable and will obviously be of importance only at frequencies where the inertial forces become comparable with the resistive forces on the electron. The formulae obtained by Drude explained reasonably satisfactorily the necessity for wave-lengths in the more distant infra-red where his expressions go over into those of the phenomenological theory.

In spite of the fair success achieved in a limited range of metallic properties, the simple electron gas model proved unsatisfactory in a number of respects. Chief amongst these was the inability of the theory to explain why the electrons did not contribute to the specific heat of a metal, the measured values agreeing quite reasonably at normal temperatures with the law of Dulong and Petit which will hold when the thermal vibrations of only the bulk material are considered. Attempts to adapt the free electron gas model to provide the required properties were not successful and it was not until 1928 that the application of wave mechanics to the problem by Sommerfeld (1928) provided an explanation.

By that time, a considerable amount of information on the optical properties of metals had been gathered experimentally. Measurements of the reflecting power of a large number of metals in the visible and ultra-violet had been made by Coblentz and his associates, (Coblentz 1906 1911, 1920, Coblentz and Hughes 1924, Coblentz and Stair 1929) while, in

the infra-red, measurements had been extended to high temperatures by McCauley (1913) who calculated the reflecting power of platinum from its emissivity. The general picture of the wave-length variation was of a fairly uniform decrease of reflectivity towards the ultra-violet for most metals with a tendency towards conformity with the Drude relation in the far infra-red. The fall in the reflectivity towards the ultra-violet culminates, as was shown by Wood (1933) for the alkali metals, in actual transparency for wave-lengths shorter than a critical value. Other features not explained at that time included the actual value of the reflectivity in the visible and near infra-red which were always lower than the predicted figures even although account were taken of inertial effects. More or less narrow bands of poor reflectivity had been observed for many metals at various wave-lengths from the ultra-violet for silver, the blue visible for copper and gold and the near infra-red for zinc. Also, although the wave-length variation of reflectivity predicted by the Drude treatment was followed reasonably closely, the predicted temperature change was not observed. Indeed, a temperature variation opposite in direction to that predicted by Drude was observed by Weniger and Pfund (1919) who distinguished between two regions in one of which the results followed the electron gas theory and in the other were governed by some different mechanism. The effect of temperature on the ultra-violet absorption band of silver had been studied by Selincourt (1925) who came to the conclusion that it could be accounted for solely by changes in the strength of the lattice binding. One phenomenon as yet unexplained is the minimum in the infra-red reflectivity of platinum at high temperatures noticed by McCauley. Apart from the behaviour in the middle and far infra-red, the theoretical interpretation of most of the above results remained obscure

on comparison with the Drude theory.

The Sommerfeld theory considered the metal to constitute a uniform potential well in which the electron is confined. Assigning to the electron the de Broglie wave-length appropriate to its velocity, the stationary energy states for the electron will correspond to standing waves resulting from reflection of the electron waves at the boundary of the metal and the energy spectrum will be a series of discrete levels. However, in addition to this model, the all-important assumption was made that the electrons obey Fermi-Dirac statistics, implying that the number of electrons which can occupy any energy state is limited to two with opposite spins. The electrons in a metal will thus fill up the available energy states, two at a time, until the top of the distribution is reached when all the electrons are placed. This immediately resolves the most pressing difficulty about the metallic specific heats as only the electrons near the top of the energy distribution will normally be able to absorb energy since only there are there neighbouring empty states to which they can be excited. This leads to a specific heat term for the electrons which is proportional to the first power of the temperature and this is, except at very low temperatures, completely overwhelmed by the specific heat of the bulk material which is following the third power of the temperature over a fairly large temperature range. Since almost all the available electronic energy states are occupied, the assembly is highly degenerate and it is only at very high temperatures that the departure from the zero temperature distribution becomes significant. It is therefore assumed that all the electrons available for conduction processes have the same energy, that appropriate to the top of the zero temperature distribution.

The wave-mechanical approach was almost immediately extended to

the case of a periodic lattice field by Bloch (1928). The result of this is to spread out each electronic energy level of the isolated atom into a band of energies. It affects the deep X-ray levels least but the broadening increases with the principal quantum number of the level until the bands may overlap. The effect on the individual electrons is to specify the energy for each electronic momentum vector. This leads to ranges of energy to which there correspond no real momentum values and these are regarded as forbidden energies. The theory thus makes clear the distinction between conductors and insulators. Non-conductors are regarded as substances in which there are just enough electrons to fill the topmost energy band, making it impossible for an applied electric field to cause any electronic transitions to constitute a current since there are no vacant states to which they can be transferred. In metals, on the other hand, it is supposed that the top of the energy distribution occurs in the middle of a band of allowed energies and transitions can take place giving rise to a finite momentum transfer.

The Bloch treatment leads to the conclusion that an electron can move through a perfect lattice without dissipation of energy so we must regard the existence of electrical resistance as the result of departures of the crystal lattice from a perfectly regular array. It is assumed that scattering of an electron wave can take place, at non-zero temperatures, by thermal vibrations of the lattice atoms, and, except at low temperatures, this contribution, proportional to the first power of the temperature, is predominant. In addition, scattering can take place as a result of static imperfections in the lattice such as impurity centres, interstitial atoms, vacancies, dislocations and grain boundaries. The effect of temperatures on these processes will be small and, in combination,

they produce the residual resistance predominant at low temperatures.

This leads to a very convenient model for the conductivity of a metal using the concept of an electronic mean free path between scattering centres in a fashion similar to the older electron gas theories. The mean free path is more logically introduced through the relaxation time which is that time required for the distribution function for the electrons to readjust itself after a disturbance under the action of the collision mechanisms described above. The form of the relation specifying this time holds rigorously only at temperatures well above the Debye temperature where thermal scattering is predominant or well below the Debye temperature where the resistance is due largely to imperfections. However, it is a convenient assumption that the conductivity is governed throughout by a mean free path derived from this relaxation time assuming that the electron possesses the energy appropriate to the top of the Fermi distribution. In the absence of any appreciable alteration with temperature of the number of electrons available to carry the current, we assume that the temperature variation of the conductivity is governed by the mean free path. The Bloch theory also allows for the excitation of an electron from one energy band to another if it is provided with the correct amount of energy and the final result of the Bloch theory bearing on the optical properties is the use of an "effective number" of electrons available for conductivity. This is the result of a factor which takes into account the extent to which the conduction band of electrons is filled and is of considerable importance in optical properties which are dependent to a very large extent on number of electrons contributing to the reflection of radiation.

The detailed theory of the optical properties of metals based on the Bloch method was given by Kronig (1929, 1931) who gave formulae for

the optical constants covering the whole range of wave-lengths from the ultra-violet to the infra-red. However, apart from the use of the effective number of free electrons and the prediction of bands of high absorption where the energy of the incident radiation is correct for the excitation of electrons from one band to another, the theory leads to the same results as are obtained by classical methods. The purely classical approach was used by Mott and Zener (1934) who considered the behaviour of a free electron gas under the influence of alternating electric fields. Formulae result which ought to be valid over the whole wave-length range and demonstrate the existence of three regions. For wave-lengths shorter than a critical value in the ultra-violet, the conditions are governed wholly by relaxation processes and the metal will be transparent for angles of incidence less that a given value. For wave-lengths greater than another value, usually far in the infra-red, relaxation effects are negligable, the reflectivity depends entirely on the d.c. conductivity and the Drude relation is obeyed. In the region intermediate between these two wave-lengths both relaxation and resistive processes are important and no approximations can be made. Coupled with the explanation of the internal photo-electric absorption bands, this treatment gave a reasonably adequate description of the observed phenomena in general. In particular, the calculated ultra-violet wave-lengths for the onset of transparency agree remarkably well with those observed but when the situation in the visible and near infra-red came to considered in detail, the agreement became less satisfactory. Very soon after the publication of Kronig's work, Hurst (1933) claimed that emissivity work on copper and nickel showed that the original Drude formula, although not completely satisfactory, fitted the results better than the Kronig theory. This is borne out by all the work

done in this wave-length range and the conclusion is that absorptivities predicted by all the theories are much too low. This was attributed to the presence of a surface layer of metal of resistivity much higher than the bulk material and experiments on the mechanism of polishing were taken as evidence for this.

It had been shown originally by Beilby (Aggregation and Flow in Solids) that polished metal surfaces are formed, when the polishing is mechanical, by plastic flow of the metal, smoothing out irregularities and covering over scratches. This will result in the formation of a surface layer of metal which is in a severely work hardened and probably amorphous state and this can be expected to have a much higher resistivity than the bulk metal. A value of the reflectivity lower than that calculated is therefore likely and Lowery and Moore (1932) and Lowery, Wilkinson and Smare (1936) in investigating the influence of surface finish on reflectivity, did obtain reduced reflectivity on burnished surfaces. However, this cannot be the complete explanation of the anomalously low reflectivities because some of the experiments involved were done at high temperatures where recrystallisation could reform a uniform lattice structure even in a highly distorted surface layer. Further evidence for the decrease of reflectivity resulting from internal strain comes from experiments on the reflectivity of alloys. Results obtained by Lowery, Wilkinson and Smare (1937) show that, in the α phase of brass, where the zinc atoms occupy lattice positions but lead to a stressed lattice, increasing zinc content leads to uniformly decreasing reflectivity but this does not help to explain the difficulties where pure, stress-free samples are concerned.

As has been mentioned above, the question of the temperature variation of reflectivity is a difficult one and, unfortunately, the newer

theories do little to clarify the situation. Although different trends with temperature have been reported, the general conclusion was that the optical properties were almost independent of temperature and this fact was used by Mott and Zener to substantiate their argument that the reflectivity is governed by a surface layer with an anomalously high resistance independent of temperature. This is not in contradiction with the temperature dependence of the reflectivity minimum in silver which had been studied by Selincourt and Rayleigh (1930) since this absorption results from electronic excitation rather than resistive damping but the high temperature measurements do not support it. Measurements by Shubert (1937), Reid (1941) and Hurst (1933) provide information on the breakdown of the Drude relation and the results have led them to divide the wave-length range into two parts, one long wave-length "electrical" region where the classical results hold and an "optical" region where the optical properties are independent of temperature or even have a temperature coefficient different in sign from that expected. These regions should presumably be identifiable with two of the regions predicted by the Mott and Zener theory but the measured values of reflectivity still show that the theory in the "optical" region is far from satisfactory.

This distinction between the two spectrum regions has been carried further by Price (1947) and Weil (1947). On the basis of reflectivity and emissivity measurements on a number of metals at high temperatures they point out that a very small positive temperature coefficient of reflectivity can be obtained in the optical region so that, in transition to the negative temperature coefficient required by the Drude relation at long wave-lengths, there must be an "X"-point, a wave-length for which the temperature coefficient of reflectivity is zero. This is claimed by Price

to be a fundamental constant for each metal but little agreement between the wave-lengths of the X-points obtained by different methods is found. The theoretical treatments of both Price (1949) and Weil (1948) aim at a simplification of the reflectivity formulae obtained from the optical constants and the search for stationary points of the reflectivity. An explanation is suggested by Price in terms of the effects of the bound electrons and suggests a complete revision of dispersion theory. However, it is pointed out by Weale (1949) that stationary points follow quite naturally from the classical treatment, or, more satisfactorily, from the Zener method. It is thus unnecessary to postulate any further physical effects and the only addition required to the Mott and Zener treatment is the explanation of the anomalously high surface resistivity.

So far we have dealt only with optical frequencies since, on the basis of the classical, electron gas model, it is only there that effects resulting from the nature of the electrons become important. The use of radio frequencies should not lead to anything new as, although the currents may be confined to a surface layer, inertial effects are negligable and the phenomenological treatment should hold very exactly. However, experiments by London (1940) on the radio-frequency resistance of tin at low temperatures gave anomalous results quite separate from the superconductivity phenomena under investigation. He found that the resistance of normal tin at about 1,500 mc./sec. frequency and liquid helium temperatures was many times greater than the value expected from the d.c. conductivity. London suggested that this could be due to the mean free path of the conduction electrons being comparable with, or greater than, the penetration depth of the radiation fields. This would mean that an electron, reflected from the surface of the metal, would, if we assume the period of vibration of

the radiation to be large compared with the free time of the electron, be moving in a rapidly diminishing electric field resulting in an effective increase in resistivity. Further experimental work was done on the high frequency conductivity of normal metals by Pippard (1947). Working over a temperature range down to 2°K, he showed that the high frequency conductivity, instead of increasing continuously with the d.c. conductivity as the temperature was reduced, tended to a constant value, illustrating the restriction of conductivity as the mechanism suggested by London became effective.

The matter was treated theoretically by Reuter and Sondheimer (1948) who obtained expressions for the high frequency conductivity without making the assumption that the electron moved in a spatially constant field. The result, in the optical region, is an expression for the ratio of the anomalous skin resistance to the classical value, which acts as a correction factor to be applied to the classical curve of reflectivity against wave-length or temperature. The variation of this correction factor with wave-length or temperature results in a minimum of reflecting power, the conditions on one side of the minimum being classical and on the other side governed by inertial effects. The value of the correction factor is largest for long wave-lengths and low temperatures but is still finite for the appropriate frequencies even at room temperature.

Thus the complete picture of the variation of reflecting power of normal metals with wave-length expected from all the above considerations is of a transparency region for short wave-lengths, a classical region of long wave-lengths and an intermediate region with, superimposed on this, regions of poor reflectivity due to internal photoelectric absorption and any restriction of conductivity by the anomalous skin effect. Temperature

ought to have the full classical effect through the resistivity on the Drude region, should have a smaller but still definite effect on the intermediate region and should have progressively smaller effect as the wave-length is reduced towards the ultra-violet transparency region. The main effect of temperature can thus be expected to result from the creation of a situation in which the anomalous skin effect will be operative. The problems outstanding are to explain why the absorption in the visible and near infra-red is higher than is indicated by the d.c. conductivity and why the expected temperature coefficient of reflectivity is not observed.

The question as regards superconductors is rather different. Apart from normal temperature effects a finite change in reflectivity at the superconducting transition can be expected on the basis of the theories discussed above. In the infra-red, at least, it could be argued that the zero value of resistivity should lead to perfect reflectivity. However, when the situation is considered in detail, we see that the gap in the electronic energy spectrum postulated to account for superconductivity is so much smaller than the energy of the incident photons in the visible and infra-red that its presence may not effect the optical properties at all. Thus, in two attempts to detect any change in reflectivity at the superconducting transition, both failed. Daunt, Keeley and Mendelssohn (1937) used an absorption method in the infra-red and Hirschlaff (1937) measured the reflectivity directly in the visible and near infra-red. It was concluded from these experiments that the effect, if it existed, was less than 0.5%.

The issue was revived by the work of Pippard (1947, 1950) on the radio-frequency resistance of superconductors. Normally the presence of super-currents ensures that no electric field penetrates into the super-

conductor and the existence of the remaining normal electrons cannot be demonstrated. A magnetic field, however, can penetrate to a depth of about 10^{-5}cm. and, if this can be caused to alternate, an electric field can be generated inside the penetration depth of the magnetic field. This is the mechanism first proposed by London and developed by Pippard in the study of the super-conducting transition at radio-frequencies. These experiments verify the existence of resistivity in the sample even below the transition temperature giving a smeared transition curve of resistance against temperature. The extent of this smearing increases as the frequency of the fields is increased and presumably continues to be smoothed with decreasing wave-length until, in the infra-red and visible, no change is detectable. It would, therefore, be of interest to obtain information about the intermediate region and this is the problem for which the present work was undertaken. The aim was to use long infra-red wave-lengths in an attempt to obtain a transition curve intermediate in form between the unchanged optical reflectivity and Pippard's smoothed transitions.

Although it was not possible in the present case to complete this plan, a similar experiment was done by Ramanathan (1952). He used the same type of apparatus as in the Daunt, Keeley and Mendelssohn experiment with room temperature radiation peaked at a wave-length of 10μ as a source and found that any effect at the transition must be less than 5%. Measurements on normal metals showed that, even taking into account the Reuter and Sondheimer correction for the anomalous skin effect, the absorption was much greater than expected. This merely confirms all previous work but shows that there must be some mechanism, still obscure, which is limiting the high-frequency conductivity.

As it proved impossible to study superconductors, an investigation

of the reflecting power of normal metals was undertaken over a temperature range between 20°K and room temperature. This temperature range does not appear to have been used to any extent in optical work and, as the apparatus was designed to measure small changes in reflecting power, it was felt that the undecided question of the temperature variation of reflectivity could profitably be investigated. The metals used were tin, copper and silver. Tin was chosen as it was hoped later to extend the results to the superconducting case. Silver was suitable because of its amenability to theoretical treatment and copper was taken as an example of an easily accessible photoelectric absorption band. It was found that the biggest changes of reflectivity with temperature occurred in the visible and near infra-red and attention was concentrated on this region.

CHAPTER II

The study of the optical properties of metals is interesting on two accounts. Firstly, because of the high damping of an electro-magnetic wave in a metal, only a very thin layer of metal is investigated and this is useful for studying much thinner layers than can be prepared experimentally and can be used to investigate purely surface phenomena. Secondly, the nature of the conduction electrons can be shown up much more clearly than in d.c. conductivity experiments by the way they react under alternating fields. As we shall be largely concerned in optical experiments with divergence from the simple d.c. conductivity theory resulting from the detailed nature of the electrons, it is important to see how far the phenomenological theory is valid.

For an isotropic, homogeneous conductor, Maxwell's equations describing the electromagnetic field can be written:-

$$\text{curl } \underline{H} = 4\pi (\underline{j} + (1/4\pi c.)\, \dot{\underline{D}}) \qquad (1)$$

$$\text{curl } \underline{E} = -(1/c.)\, \dot{\underline{B}} \qquad (2)$$

$$\text{div } \underline{B} = 0 \qquad (3)$$

$$\text{div } \underline{D} = 4\pi\rho \text{ which we consider to be zero} \qquad (4)$$

To these must be added the constitutive relations specifying the properties of the material:-

$$\underline{D} = K\underline{E} \qquad (5)$$

$$\underline{B} = \mu \underline{H} \qquad (6)$$

$$\underline{j} = \sigma \underline{E} \qquad (7)$$

where $\underline{H}$ is the magnetic field inside the medium, $\underline{E}$ the electric field, $\underline{j}$ the current, $\underline{B}$ the magnetic induction, $\underline{D}$ the electric displacement, c the ratio of the electromagnetic to the electrostatic units of charge, ρ the

charge density, K the dielectric constant of the medium, μ the permeability (assumed to be unity) and σ the conductivity. For the present we shall assume the correctness of the equations 5, 6 and 7 and determine the behaviour of the model thus specified. We shall discuss the nature of the breakdown later.

By eliminating $\underline{E}$ and $\underline{H}$ in turn from equations 1 and 2 we can obtain the equations:-

$$\nabla^2\underline{H} = (K/c^2).\ddot{\underline{H}} + (4\pi\sigma/c^2).\dot{\underline{H}}$$
$$\nabla^2\underline{E} = (K/c^2).\ddot{\underline{E}} + (4\pi\sigma/c^2).\dot{\underline{E}} \qquad (8)$$

We see from these that the fields will form a wave travelling with velocity $c/\sqrt{K}$ as in the case of an insulator but, in addition, the terms in $\dot{\underline{E}}$ and $\dot{\underline{H}}$ show that the wave is damped. The analysis is simplified if we assume that the wave is plane polarized with components E_y, H_z travelling in the positive X direction. Equations 8 must be satisfied by each component and equations 1 and 2 can be written:-

$$-\frac{\partial H_z}{\partial x} = \frac{K}{c}\frac{\partial E}{\partial t} + \frac{4\pi\sigma}{c}E_y$$
$$\frac{\partial E_y}{\partial x} = -\frac{1}{c}\frac{\partial H_z}{\partial t} \qquad (9)$$

The nature of the equations 8 and 9 suggests that the expressions for E_y and H_z should be of the form:-

$$E_y = ae^{i\omega(t-\frac{p x}{c})}$$
$$H_z = be^{i\omega(t-\frac{p x}{c})}$$

where ω is the angular velocity of the wave vector, a and b are constants and p is the ratio of the wave velocity in a vacuum to the velocity in the medium. Since we have seen that the wave is damped, p must be of the form n - ik so that we can write:-

$$E_y = ae^{-\frac{\omega k x}{c}}\ e^{i\omega(t-\frac{n x}{c})}$$

indicating that the amplitude of the wave will decrease exponentially with distance into the metal. Thus, since n is the normal refractive index and k governs the decay of a wave, n and k determine the optical properties of the metal completely.

The actual values of n and k given by the Maxwell model can now be obtained by substitution of the above expressions for E and H into equations 9. Separating real and imaginary parts we find:

$$n^2 - k^2 = K$$

$$2nk = 2\sigma T$$

where T is the period of the wave. Hence:

$$\left.\begin{aligned} n^2 &= \tfrac{1}{2}\left\{\sqrt{K^2 + 4\sigma^2T^2} + K\right\} \\ k^2 &= \tfrac{1}{2}\left\{\sqrt{K^2 + 4\sigma^2T^2} - K\right\} \end{aligned}\right\} \qquad (10)$$

In optical work we are largely concerned with the actual values of n and k or $n^2 - k^2$ and 2nk since they are the quantities most suitable for comparison with theory. However, because of the convenience of reflectivity measurements, it is desirable to obtain an expression for the reflectivity R in terms of n and k.

Consider a plane polarised wave with components E (ɣ) and H (ƶ) travelling in the X-direction into the metal of refractive index p. Let the incident wave be given by: $E_1 = a\, e^{i\omega(t - x/c)}$ $H_1 = b\, e^{i\omega(t - x/c)}$

the transmitted wave by: $E_2 = a\, e^{i\omega(t - px/c)}$ $H_2 = b\, e^{i\omega(t - px/c)}$

and the reflected wave by: $E_3 = a\, e^{i\omega(t + x/c)}$ $H_3 = b\, e^{i\omega(t + x/c)}$

The substitution to give the expressions for $n^2 - k^2$ and 2nk also lead to the result that, in the metal:-

$$b_2 = pa_2$$

while in free space:-

$$a_1 = b_1 \qquad a_3 = b_3$$

The boundary conditions that the tangential components of E and H should be continuous at the metal surface leads to the relation between the amplitudes:-

$$a_1 + a_3 = a_2 \quad \text{and} \quad a_3 - a_1 = p\ (a_1 + a_3)$$

The reflecting power is defined by:-

$$R = \text{reflected intensity/incident intensity}$$

and so

$$\begin{aligned} R &= a_3\, a_3^*/a_1\, a_1^* \\ &= \frac{(p-1)(p^*-1)}{(p+1)(p^*+1)} \\ &= \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \end{aligned} \tag{11}$$

This result, as far as the part containing n is concerned, is perfectly general and holds for all types of wave motion. It involves the particular model of the conduction processes only through the extinction coefficient k and we see that this does not influence the reflecting power strongly. The formula is therefore of fairly general validity and we shall assume that it holds even when we are considering models which give results not in agreement with the Maxwell theory.

With the values of n and k given by 10, the formula for R is perfectly rigorous within the framework of the Maxwell theory but is obviously cumbersome and it is customary to note that, for low frequencies of radiation and good conductors:-

$$2\sigma T \gg K$$

This certainly restricts the scope of the treatment but, for copper at room temperature with a wave-length of 1μ, it is true to within .02%. The formulae 10 then simplify to:-

$$n^2 = k^2 = \sigma T$$

and the reflectivity is given by:-

$$R = \frac{2\sigma T - 2\sqrt{\sigma T} + 1}{2\sigma T + 2\sqrt{\sigma T} + 1}$$

or, assuming $\sigma T \gg 1$:-

$$R = 1 - 1/\sqrt{\sigma T} \qquad (12)$$

This is the Drude relation for the reflectivity giving a direct dependence of the reflecting power on the conductivity. It ought to hold down to near infra-red wave-lengths for good conductors but it was apparent from even the earliest experiments of Hagen and Rubens that the relation was not obeyed down to the predicted limit and that much greater wave-lengths were required to give agreement. The source of this discrepancy is obviously the failure of relation 7. This equation expresses the condition that the carrier of the current should follow the applied field exactly and in a free electron theory of conduction where a finite mass is ascribed to the electrons, the response is bound to be limited by inertia. The breakdown is even more complete in the case of electrolytes where the carriers have relatively enormous masses and do not respond to frequencies much higher than those of the audio band.

To enlarge the scope of the theory it is necessary to discard the assumption of a smoothed, d.c. conductivity and consider the actual behaviour of the electrons under alternating fields as was done by Mott and Zener (1934). We regard the reflectivity of the metal as due to the oscillation and consequent re-emission of the free electrons under the incoming radiation fields. The optical properties will depend on the extent to which the electrons respond to the fields and so will be obtainable from the polarisation. For, if we write:-

$$\text{curl } \underline{H} = 1/c\ \dot{\underline{D}}$$

$$\underline{D} = \underline{E} + 4\pi \underline{P}$$

where $\underline{P}$ is the polarisation of the electron gas resulting from the

radiation fields, then:-

$$\text{curl } \underline{H} = 1/c\ (1 + 4\pi P/E)\ \underline{E}$$

since $\underline{P}$ and $\underline{E}$ are assumed to be parallel. Now this is the normal Maxwell equation for a material of dielectric constant $1 + 4\pi P/E$ and the normal development then leads to a refractive index:-

$$p^2 = 1 + 4\pi P/E \qquad (13)$$

Although this has been derived subject to the conditions that $\underline{P}$ and $\underline{E}$ are parallel and so p either real or imaginary, we shall assume that it continues to be valid if there is a dissipating factor giving a phase difference between $\underline{P}$ and $\underline{E}$ and resulting in a complex value for p. It will serve as the means of obtaining expressions for the optical properties having calculated the polarisation for any particular model.

In the free electron gas model we consider first a single electron of mass m and charge e oscillating under the influence of the electric field of the incoming radiation. We ignore the Lorentz force resulting from the motion of the electron in the magnetic component of the radiation fields. It is assumed that the motion of the electron in the metal is governed by a free time τ which is considered to be the same for all the electrons. Now, we know that, for the static case, the formal result of this is a conductivity σ given by:

$$\sigma = ne^2\tau/m$$

so that, considering this to be equivalent to the general expression for the current:-

current density

$$\underline{j} = ne\underline{v}$$

where n is the number of free electrons per unit volume and $\underline{v}$ is their velocity, we can say, without enquiring too closely into the precise meaning of τ, that the velocity of the electron under the radiation field

will be:-

$$\underline{v} = (e\tau/m.)\,\underline{E}$$

The equation of motion of the electron under the radiation field which we shall assume to be given by:-

$$\underline{E} = E_o e^{i\omega t}$$

is then:-

$$m\ddot{x} + (m/\tau) \cdot \dot{x} = eE = eE_o e^{i\omega t} \qquad (14)$$

The first of these terms gives the effect of the inertia of the electrons and will be predominant at high frequencies where $\omega \gg 1/T$. The second takes account of resistive damping and will govern the behaviour at low frequencies where $\omega \ll 1/T$. To treat the general case we must obtain the complete solution of equation 14. The complementary function is:-

$$x = e^{-t/\tau} - 1$$

which can be ignored as we are seeking only alternating solutions. The normal methods of solution then give for a particular integral:-

$$x = \frac{eE_o e^{i\omega t}}{m\omega(i - \omega\tau)}$$

This, incidentally, gives the expression for the conductivity at any frequency:-

$$\sigma(\omega) = \frac{ne^2\tau}{m(1 + i\,\omega\tau)}$$

The polarisation of the electron gas under the radiation field will then follow from the displacement by:-

$$P = nex$$

Thus:-

$$P = \frac{ne^2E\tau}{m\omega(i - \omega\tau)}$$

and so the refractive index is given by:-

$$p^2 = 1 + \frac{4\pi ne^2\tau}{m\omega(i - \omega\tau)}$$

Thus, comparing real and imaginary parts:-

$$n^2 - k^2 = 1 - \frac{4\pi ne^2 \tau}{m(\omega^2 + \frac{1}{\tau^2})}$$

$$2nk = \frac{4\pi ne^2}{m\omega\tau(\omega^2 + \frac{1}{\tau^2})} \qquad (15)$$

In principle we can now solve for n and k and use the expression for the reflectivity to obtain the value for the reflectivity on the electron gas model. This will obviously lead to very complicated functions and the behaviour of the reflecting power can be seen better by considering various wave-length ranges in which different mechanisms are predominant. Two regions are definitely specified.

I) Inertial term predominant.

This will occur when:-

$$m\omega^2 \gg m\omega/\tau$$

ie. $\omega \gg 1/\tau$

Thus, for ultra-violet wave-lengths the behaviour of the system will be described by:

$$m\ddot{x} = eE_0 e^{i\omega t}$$

or $$x = -eE/m\omega^2$$

Hence $$P = -ne^2E/m\omega^2$$

and so $$p^2 = 1 - 4\pi ne^2E/m\omega^2$$

The optical properties are thus determined by the quantity $4\pi ne^2/m\omega^2$ If it is less than unity, the refractive index is real and the metal is transparent for normal incidence. If it is greater than unity, the refractive index is imaginary and the metal is perfectly reflecting. This condition is to be identified with the behaviour of the alkali metals in the ultra-violet which had been observed by Wood (1933).

II) Resistive term predominant.

This is the case for $\omega \ll \frac{1}{\tau}$ and so, for the infra-red, the equation reduces to:-

$$(m/\tau)\,\dot{x} = eE_0 e^{i\omega t}$$

ie. $$x = ie\tau/m\omega E$$

$$P = ine^2\tau E/m\omega$$

Thus $$p^2 = 1 + 4\pi ine^2\tau/m\omega$$

and, separating real and imaginary parts:-

$$n^2 - k^2 = 1$$

$$2nk = 4\pi ne^2\tau/m\omega$$

This is equivalent to:-

$$nk = \sigma T$$

and $$nk \gg n^2 - k^2$$

These are the conditions for the validity of the Drude relation which we have discussed above. Thus, in the limit of long waves, the formulae derived from the electronic model reduce, as expected, to those obtained from the Maxwell model.

III) Intermediate region.

When the two terms are of equal importance no approximations can be made in the original formula, the full solution must be retained and the optical constants are as given by equations 15. However, the derivation of the formulae involved the assumption that the dissipative forces acted through a smoothed, d.c. resistivity. We are now dealing with the state of affairs in which the period of the wave is less than the free time of the electrons and the precise mechanism of the resistance is possibly more important than before. It may, therefore, not be valid to approximate, as Mott and Zener do, to the case where $\omega \gg \frac{1}{\tau}$ and to write the equations:

$$n^2 - k^2 = 1 - 4\pi ne^2/m\omega^2$$
$$2nk = 4\pi ne^2/m\omega^3\tau \qquad (16)$$

The wave-length for which $\omega = \frac{1}{\tau}$ lies, generally, far in the infra-red so that, in the visible, the conditions are that, during a number of oscillations under the field, the motion of the electron will be resistance-free but a collision will occur in some period, the number of free periods being a measure of the amount by which the free time of the electrons exceeds the period of the wave.

To derive the properties of this model we continue to assume that all the electrons have the same free time τ so that, in one period of the wave, a fraction T/τ of the electrons will experience a collision. The remaining $1 - T/\tau$ will follow the resistanceless case. For the latter, the polarisation P is:

$$P = -n(1 - T/\tau)e^2E/m\omega^2 \qquad (17)$$

where, as before, n is the total number of electrons per unit volume contributing to the polarisation.

In the former case, the circumstances are that, somewhere, during the period, the electron will experience a collision which will reduce to zero the velocity acquired under the influence of the radiation fields. They will then be accelerated again and continue the oscillation as before, except that they will lag behind those which did not experience a collision.

Let an electron of charge e and mass m, oscillating under an electric field $E = E_0 e^{i\omega t}$ start from $x = 0$ at $t = 0$. Its equation of motion is:-

$$m\ddot{x} = eE_0 e^{i\omega t}$$

So $$\dot{x} = (-eE_0/im\omega)\, e^{i\omega t} + eE_0/im\omega$$

and $$x = (-eE_0/m\omega^2)\, e^{i\omega t} + (eE_0/im\omega)\, t + eE_0/m\omega^2$$

Let a collision occur at $t = t'$ which reduces to zero the velocity acquired under the field but does not alter its displacement. The equation of motion with $x = 0$ at $t = t'$ leads to:

$$x = (-eE_0/m\omega^2)e^{i\omega t} + (eE_0/im\omega)e^{i\omega t} \cdot t + (eE_0/im\omega)t'(1-e^{i\omega t}) + eE_0/m\omega^2$$

Since the time of the collision is arbitrary we require the average of this expression as t' varies from 0 to t. This gives:-

$$x = (eE_0/m\omega)(\omega t/2i - e^{i\omega t} - (1/i\omega t)e^{i\omega t} + 1/i\omega t)$$

Since this is not a simple function of E such as we have had before, it is not possible to derive directly a value for P/E. One simplifying assumption is to consider the values of the polarisation and field at $\omega t = \pi/2$.

$$x_{\pi/2} = (eE_0/m\omega^2)(2/\pi + i\,(1 - \pi/4 + 2/\pi))$$

So
$$P_{\pi/2} = (nTe^2E_0/4\pi m\omega^2)(2/\pi + i(1 - \pi/4 + 2/\pi))$$

Adding together the two parts of P/E and substituting to obtain the refractive index we find, on separating real and imaginary parts:-

$$\begin{aligned} n^2 - k^2 &= 1 - (4\pi ne^2/m\omega^2)(1 - 1/\omega\tau\ (\pi^2/8 - 1)) \\ 2nk &= 4\pi ne^2/m\omega^3\tau \end{aligned} \qquad (18)$$

This shows that the effect of considering the free path is merely to alter the dielectric term. The absorption remains unaltered as might be expected since it depends, presumably, only on the number of collisions occurring per second which will be independent of the refelctivity mechanism.

Since, for the visible, T is much less than τ for normal conditions, the formulae 18 should hold. The only region not covered rigorously by the foregoing theory is that where T is approximately equal to τ. We can then assume that neither the smoothed d.c. case or the high frequency case just considered will hold and we cannot expect to be able to extend the range of validity of the high frequency treatment up to $T = \tau$ and beyond because no account is taken of the possibility of the electron

experiencing more than one collision in one period of the wave. It is difficult to imagine precisely what the state of affairs actually at $T = \tau$ is but, again, we cannot expect any anomalous absorption since the total number of collisions occurring per second will still be the same.

The general picture of reflectivity derived from the free electron gas model is thus of purely dielectric behaviour below a certain wave-length λ_0, a sudden rise in reflectivity, as the wave-length is increased, to a value very near 100%, and, eventually, a purely classical region where the Drude relation holds. In the intermediate region the absorption should vary as $1/\omega^3$ at the low wave-length end and this will gradually become less important as resistive effects become predominant with increasing wave-length.

The effect of temperature on the short wave-length behaviour is negligable since the inertial effects are predominant and ought to increase gradually as the influence of the damping term increases until it has its full effect in controlling the reflectivity in the Drude region.

The use of a wave mechanical model does not lead to any new results if a uniform potential inside the metal is assumed and formulae 15 still hold. However, the use of the periodic lattice field introduced by Bloch makes several very important changes which alter the optical properties directly. The first follows from the fact that the acceleration of an electron while moving through a periodic lattice field is not the same as if it were moving in a region of constant potential. The correction is made by using either an "effective mass" of the electron or an "effective number" of free electrons. This certainly affects the optical properties into which the number of free electrons enters directly but the correction is a constant, numerical one and no important new phenomena emerge. The

second change is the result of considering the polarisation of the lower levels of electrons in the bound shells and also polarisation resulting from the oscillatory nature of the electron's behaviour in a periodic lattice. These will make a certain contribution to the polarisation but the effect is negligable at low frequencies for both cases and, for the second case, also at very high frequencies.

Much more important than either of the foregoing is the third result of considering a periodic lattice field. One of the main consequences of the Bloch theory is that the energy of an electron is specified by its wave number to the extent of having one of several values given by a multi-valued curve. The theory allows for a finite transition probability between states with the same wave number resulting in the absorption or emission of a definite amount of energy. If radiant energy of the appropriate frequency is supplied, these transitions will result in an anomalously high absorption of energy from the wave and bands of poor reflectivity about this frequency will be observed. As none of these effects will be considered in detail, no more than this outline of their nature will be required.

The only other theoretical treatment requiring consideration is that of Reuter and Sondheimer (1948). In this, one more assumption inherent in the free electron gas model is removed for it is clear that, if the free path of the conduction electrons is longer than the penetration depth of the incident radiation fields, the full accelerating effect of the fields on an electron reflected from the surface will not be felt and this will be equivalent to an increase in skin resistivity. The nature of the breakdown of the old model is concerned with the failure of the assumption $\mathbf{j} = \sigma \mathbf{E}$ as we now have to deal with a spatially varying field. The frequency

band will be divisible into three regions: a) the low frequency region where the penetration depth is much larger than the free path and the conditions are classical, b) the high frequency region in which, although the penetration depth is small compared with the free path, the period of one oscillation of the wave fields is so short that the distance travelled by an electron in one period is short compared with the penetration depth and, again, the classical conditions hold, c) the anomalous region in which the actual distance travelled by the electron in one period of the wave is larger than the penetration depth. A simplified treatment of the case was given by Pippard (1947a) using a free electron gas model. He used the standard methods of gas kinetics and made the assumption that only those electrons which meet the surface at a small angle are effective in conduction. Fairly satisfactory agreement with Pippard's own results on the radio frequency resistance of normal metals was obtained but the rigorous solution was given by Reuter and Sondheimer.

The treatment given by Reuter and Sondheimer generalises the normal conduction theory by writing the electronic distribution function in the form:-

$$f = f + f_1(\underline{v}, z)$$

where f is the undisturbed Fermi function, f the required function giving the effect of the radiation fields, $\underline{v}$ is the electron velocity and z the distance in from the metal surface and obtaining a solution without ignoring variation with z. This means that the method is generalised to the extent of considering spatial variation of the radiation fields. The value of the distribution function can then be used to obtain the required relation between the current $\underline{j}$ and the field $\underline{E}$ from which the surface impedance Z can be determined. The solution is obtained for two different cases, a) when

the fraction p of electrons reflected from the metal surface is unity and b) when p is zero, but the difference between the results in the two cases does not appear as very significant. The case of the micro-wave region is considered in detail and the variation of the surface impedence with frequency compared with Pippard's results. This curve, which illustrates the tending of the surface conductivity to a constant value as the conduction processes are limited by the anomalous skin effect, agrees in form with that obtained by Pippard except in the case of mercury which does not tend to a constant value with decreasing temperature. However, the values found for the number of conduction electrons per unit volume, while in fair agreement with other measurements for tin, mercury and aluminum are unreasonably low in the case of copper, silver and gold. This is rather arbitrarily attributed to a surface layer of abnormally high resistivity in those three metals.

The optical region is much more difficult to deal with as no simplifying assumption about the smallness of $\omega\tau$ can be made and the result is provided only for the case p = 1. The final expression giving the extent to which the anomalous skin resistance R exceeds the classical skin resistance R_{ℓ} is:-

$$\frac{R}{R_{\ell}} = \frac{4}{\pi}\sqrt{\frac{2\alpha}{3}}\ \frac{\omega\tau\, R(I) - I(I)}{(1+\omega^2\tau^2)\sqrt{-\omega\tau + \sqrt{1+\omega^2\tau^2}}}$$

where

$$I = \int_0^\infty \frac{dt}{t^2 + i\alpha k(t)/(1 + i\omega\tau)^3}$$

and

$$k(t) = 2t^{-3}((1 + t^2)\arctan t - t)$$

R and I denote the real and imaginary parts of the integral and $\alpha = (3/2)\frac{l^2}{\delta^2}$ l^2/δ^2, where l is the electronic mean free path and δ the penetration depth, is a measure of the departure from classical conditions. The graph of R/R_{ℓ} against $\omega\tau$ gives, for each value of α, a peaked curve with a

maximum where the anomalous effects are predominant. The high values leading to the greatest divergences from classical theory occur at low temperatures but the correction is still finite, for the appropriate frequencies, even at room temperature.

An anomalous value for the optical reflectivity will follow from the high skin resistance but will be difficult to observe because, when the effect is largest, the wave-lengths involved are in the radio band and when optical frequencies are used, the anomalous effects tend to be masked by high frequency effects resulting from the short distance travelled by the electron in one period of the wave.

CHAPTER III

It can be seen from the thoretical discussion given above that the most fundamental quantities in the optical properties of a metal are its refractive index n and its extinction coefficient k from which the reflectivity can be calculated. This approach has been the one most used in the past and the constants n and k are determined from the changes taking place in polarised light reflected from the metal surface. If the incident light is plane polarised with the plane of polarisation making an arbitrary angle with the plane of incidence, both components of the light, parallel and perpendicular to the plane of incidence will suffer a phase change depending on the values of n and k and analysis of the resulting elliptically polarised light will lead to a determination of $n^2 - k^2$ and $2nk$. An alternative method which has been used more recently is to measure the reflected intensity either for two angles of incidence with a given plane of polarisation of the incident light or with two planes of polarisation for a single angle of incidence. The latter method, as proposed by Tousey, (1939) seems the better of the two but in both cases the analytical treatment is cumbersome and the values of n and k are obtained graphically.

These methods have the merit of comparative simplicity and adaptability to different conditions but suffer from the drawback that the constants of the light after reflection are seriously affected by contaminating films on the metal surface. This limits the reliability of the absolute values of the optical constants obtained by those methods but the variation with wave-length does not seem to be so seriously affected. The extinction coefficient can be determined independently from experiments

on the transmission of light through thin films of the metal but the low penetration depths in the metal necessitate films so thin that they are of doubtful structure and their thickness is very difficult to measure.

Since we must have that, for any wave-length, the sum of the reflecting and absorbing power is unity, measurements of the absorbing power can be claimed to be more accurate than reflectivity measurements as small changes, occurring equally in the reflectivity and the absorption, are proportionately much greater for the absorbing power. This is certainly true but the problem is merely transformed into one of measuring accurately the very small amounts of energy absorbed. Instead of the absorbing power it is sometimes useful to measure the emissive power. This is probably the most convenient method at high temperatures where direct measurements of reflectivity or absorbing power would be very difficult and is claimed, eg. by Hurst (1933) to be much more accurate than other methods. However, apart from the difficulties involved in maintaining a perfect emitting surface at high temperatures, the method is limited in temperature and wave-length range.

We are left with the possibility of measuring the reflecting power directly. Such a method has the advantage that any conditions eg. of wave-length or temperature can, in principle, be used but has the important drawback that, although experimental values of n and k can be used to calculate R, the process cannot be reversed to obtain n and k from R. A measurement of reflectivity is therefore useful only when the absorption is the only quantity under consideration. The principal experimental difficulties are connected with the obtaining of accurate absolute values of reflectivity as some mechanical means must be found of selecting either the direct beam from the source or that reflected from the specimen and

this may well introduce errors greater in magnitude than a small change in reflectivity which it is desired to detect. The problem of surface films remains but, since less information is required from the measurements, it is perhaps not so serious as in the polarised light methods. Another important difficulty in the case of high reflectivities is that a small change is such a small proportion of the total signal received. This can be overcome by using some method based on multiple reflections of light beams from the sample. This enhances the effect of any absorption but makes it more difficult to compare the reflected light with the incident beam. Finally, all the methods described depend directly on the stability of the source of light, the detector and the amplifying system and are liable to the full disturbing effect of any scattered radiation falling on the detector in addition to the measuring beam. However, many of the difficulties outlined above can be overcome by the use of suitable optical systems and the direct measurement of reflectivity provides a convenient and flexible approach to the study of absorption of radiation in metals.

The main aim in the design of the present apparatus was to measure small changes in reflectivity occurring as a result of temperature variation. Precise definition of the wave-length used was not regarded as of the highest importance and no attempt to study the wave-length variation of reflectivity in detail was contemplated. The important considerations were to obtain high stability to avoid making of any small temperature variation by spurious changes resulting from varying output of the source or lack of stability of the detecting and amplifying system and to eliminate, if possible, the effects of stray radiation. A further difficulty, as mentioned above, is that the small reflectivity change may be superimposed on a high absolute value of reflectivity making amplification of the

significant part difficult. It was with these considerations in mind that a double-beam balance method was chosen.

This technique was first used by Hardy (1929, 1935) and is now common in infra-red spectroscopy and in other applications involving the accurate measurement of low intensity radiation. (Brownlie 1950, Gibson 1951, Hindley and Leaton 1949, Hornig, Hyde and Adcock 1950, Rugg, Calvent and Smith 1951, Savitsky and Halford 1950, White and Liston 1950, Williams 1948). The method, in principle, is of the "sample in - sample out" type in which the beam reflected from the sample is continually compared with a reference beam by throwing them alternately on a detecting system. In the best systems it is arranged that equal intensities of the two beams results in zero signal and only one detector is used thus eliminating matching difficulties.

So as to cover the widest possible wave-length range, mirrors are used throughout and the arrangement of the optical system is illustrated in fig. 1. Light from the source is collimated using the spherical mirrors M_1 and M_2 which form a real image of the source, light from which leaves the mirror M_3 as a parallel beam. The only purpose served by the large mirrors is to create a transparent source and, to ensure effective collimation by the mirror M_3, a source small compared with the mirror is required. The collimated beam is then filtered to provide the required wave-length band and split by the double mirror M_4, one beam falling on the specimen mirror M_5 and the other on a reference mirror M_6. The reflected beams then pass through a rotating chopping wheel C which has spaces so arranged that the beams are transmitted alternately. Control of the beam intensities is achieved using aperatures in the screen B_1 B_2 whose area can be varied by movable shutters S_1 and S_2, and the beams are

OPTICAL SYSTEM

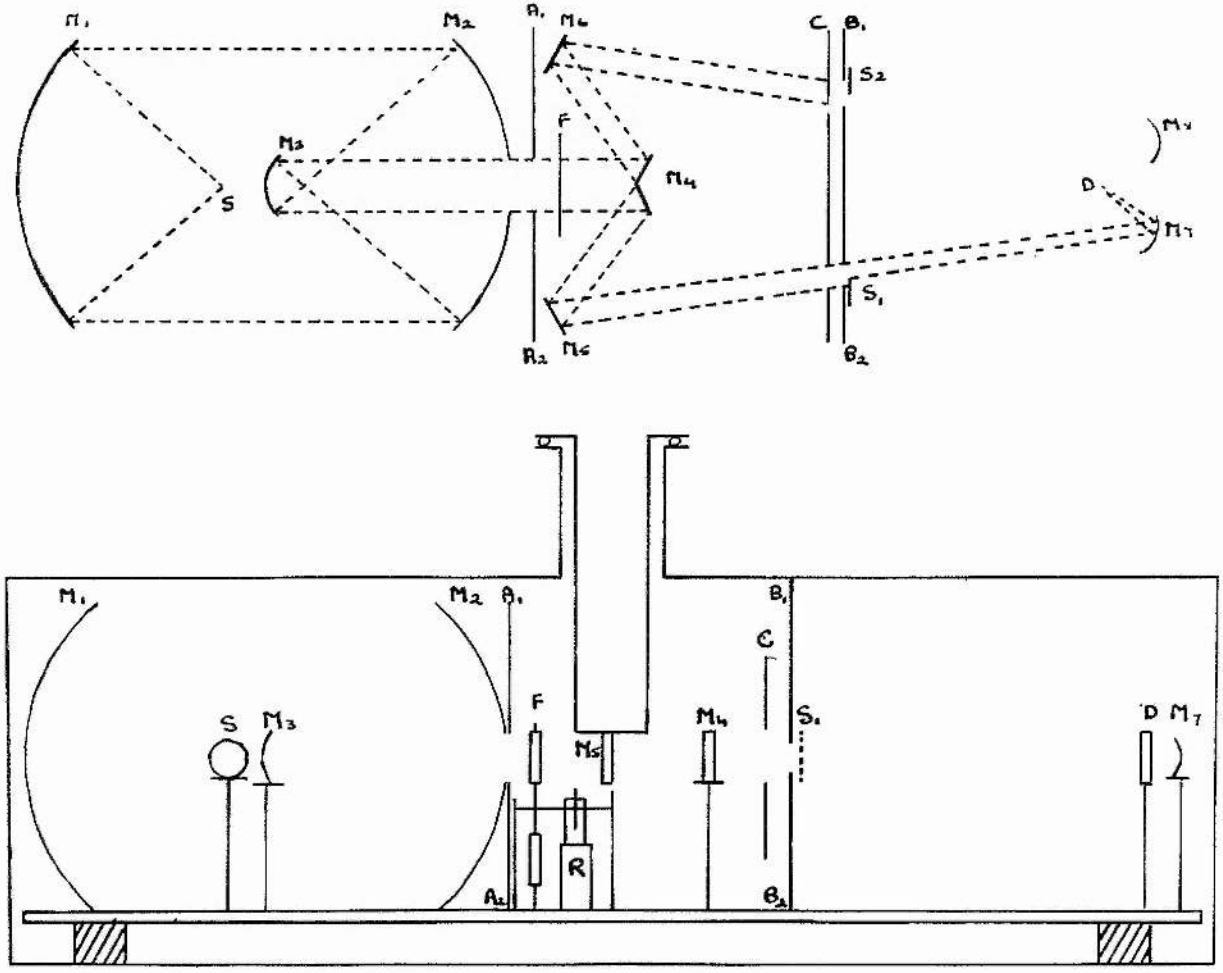


Fig. 1.

finally allowed to fall on the detector system. In the case of a detector with a very small receiver area like a thermopile, the beams can be focussed on to it using the small spherical mirrors M_7 and M_8 or the beams can fall directly on the receiver of a larger detector like a photocell. The screens A_1 A_2 and B_1 B_2 serve as diaphragms to minimise stray radiation.

With this arrangement the output from the detector consists of a d.c. voltage dependent on the absolute reflectivity of the specimen and the reference mirror and an a.c. component which is proportional to the difference in intensity between the two beams. The d.c. part is filtered off and the a.c. signal amplified electronically to be displayed on a meter thus enabling the balance point to be detected. If it assumed that no change of the reflectivity of the reference mirror occurs (or else the change, if it does occur, is known) and the system is initially balanced to give zero signal, any change in reflectivity of the specimen will be measurable from the extent of the movement of the shutter S_1 in the specimen beam which is required to restore the balance. The ratio of the new reflectivity to the old will obviously be given by the ratio of the old aperture area to the new.

Since this is a nul method, the setting of the shutter to give a balance point is independent of the actual value of quantities such as the source intensity, transmission of the optical system and detector sensitivity which affect both beams equally. The effect of scattered radiation is also eliminated as it is not chopped if the specimen and reference mirrors fill the field of view seen by the detector through the aperatures in the screen B_1 B_2, and, since only changes are measured, the initial setting of the optical system is not critical. The method also produces automatically an a.c. signal suitable for electronic amplification

thus eliminating difficulties arising from the use of contact breakers or d.c. amplifiers and, since the part of the signal corresponding to the absolute reflectivity is removed, the apparatus can be made sensitive to small changes, even although they are superimposed on high absolute values. Any desired wave-length range can be studied merely by the use of the appropriate sources, filters and detectors. The sensitivity of the apparatus is limited only by the noise level in the input circuit of the amplifier but the main disadvantage is the fact that only changes in reflecting power can be measured. In principle, an absolute determination of reflectivity could be made but the measurement would be subject to many sources of error which are eliminated when measuring changes. It would still be possible only to compare the reflectivity of the sample with that of a standard but from this absolute values could be obtained.

When using a double beam flicker method such as this, it is useful to consider the wave-form of the light pulse transmitted (Dighton, Ross and Schruffrey 1947). If this is perfectly rectangular and the pulses from the two beams fit together exactly at the detector, one after the other, no signal will result when the two intensities are equal. Even when the pulses are not rectangular, no signal results when the intensities are equal if the pulses are geometrically similar. If, however, there is any asymmetry in the wave-forms, a residual signal at the chopping frequency will remain even although the peak intensities are equal. In spite of the existence of such a balance point signal, the balance can be found by adjusting the output of the amplifier to a minimum which still occurs when the peak intensities are equal and the accuracy of the measurement is not impaired. In the case of the present apparatus, the apertures giving the final limitation to the area of the beams are circular and the edges

of the openings on the chopping wheel and the controlling shutters are linear. This results in a fairly complicated variation of aperture area exposed A with distance of the shutter edge along a diameter of the aperature x which is given by:-

$$A = 2\int a^2 - (x - a)^2 . dx$$

where a is the radius of the aperture. This gives:-

$$A = a^2 \arcsin (x - a)/a + (1/a)(x - a)\sqrt{a^2 - (x - a)^2/a^2} + /2$$

If the beam incident on the aperture is homogeneous, the transmitted intensity will follow this function. It is thus the equation for the wave-form of the transmitted pulse but the precise nature of this wave-form is not important experimentally as the harmonic terms governing the deviations of the wave-form from a perfect sine wave are greatly attenuated in the amplifying system. It does mean, however, that unequal shutter settings give rise to asymmetry which results in a balance signal. Its most important consequence is in governing the effect of the controlling shutters for the extent of opening of the shutter, which is used to measure the reflectivity, is measured in terms of the length intercepted by the shutter edge along a diameter of the aperture. The above function was evaluated for a number of values of x (table II) and a calibration curve drawn from which correction to be applied to the reflectivity readings could be obtained.

CHAPTER IV

The main consideration in designing the apparatus was to provide for a mirror surface which could be cooled and to which the radiation had access without passing through any windows. This is desirable not only for convenience in covering a large wave-length range, but also to avoid the possibility of error introduced by alteration with temperature of the transmission characteristics of the material of the window. The only alternative is to enclose the whole optical system inside the evacuated space in which the mirror and cryostat must be contained for thermal insulation and so the apparatus took the form of a cylindrical tank which could be evacuated and in which the main part of the optical system on a rigid optical bench is supported on rails. The cryostat consists of a simple tube hanging inside the tank and carrying the mirror on its outside face. This arrangement requires that a fairly large volume must be evacuated to a pressure of 10^{-4}mm. of mercury or less but it automatically solves all problems of absorption of the radiation in transmission through the system.

1) Vacuum System

The vacuum tank (figs. 2 and 3) consists of a length of copper tubing 8" in diameter and 2' 6" long. The ends are closed with brass end plates and sealed with rubber ring seals. Two 3-1/2" diameter brass tubes are mounted on top of the tank, one on each side of the axis to support the cryostats which therefore hang down inside the evacuated space clear of the walls. The mirrors are mounted on the outside surface of the cryostats, in the vacuum, so as to take their place in the optical system. The cryostats simply hang from flanged plates which rest on rubber ring

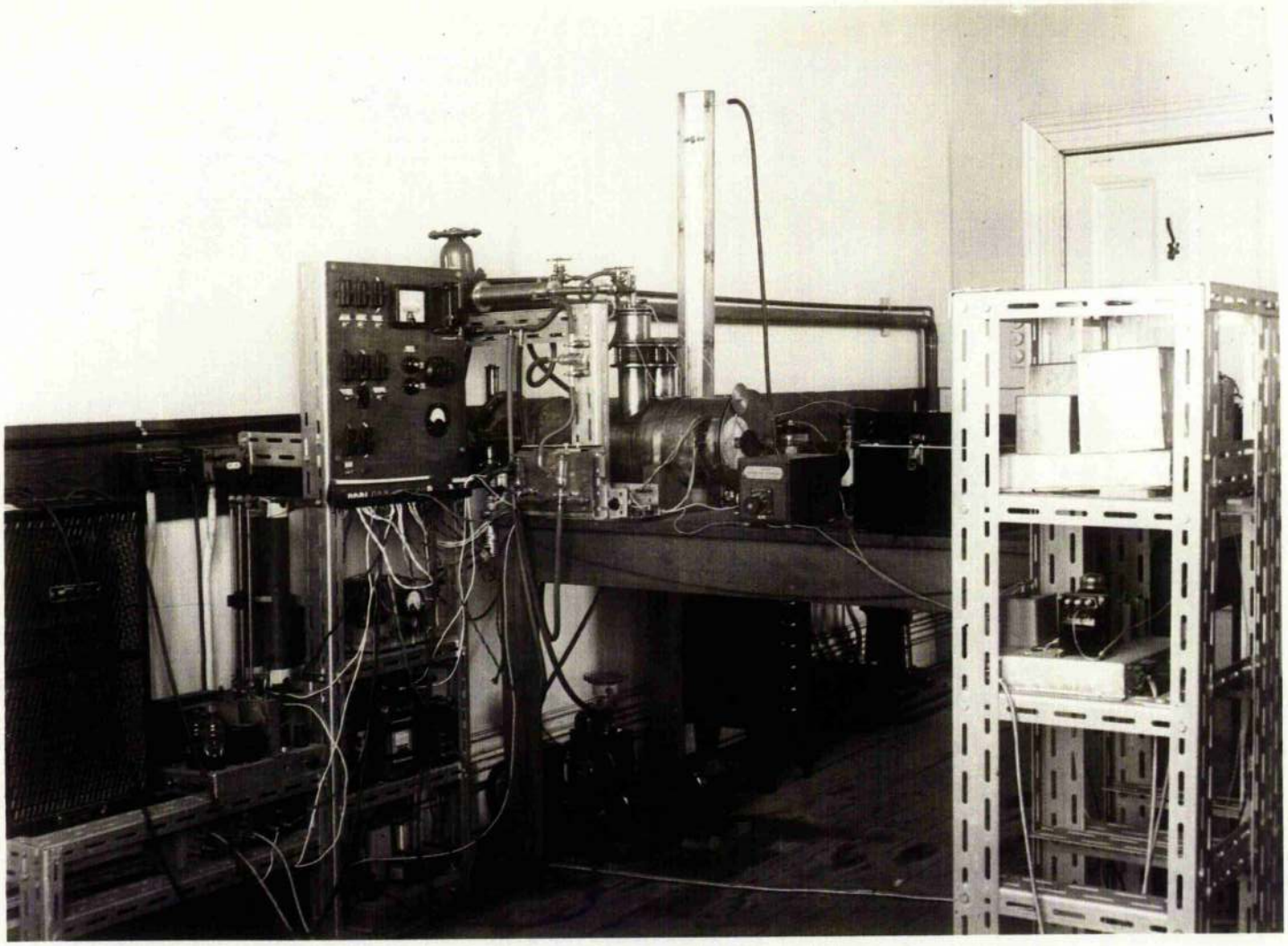


Fig. 2. General view of reflectivity apparatus

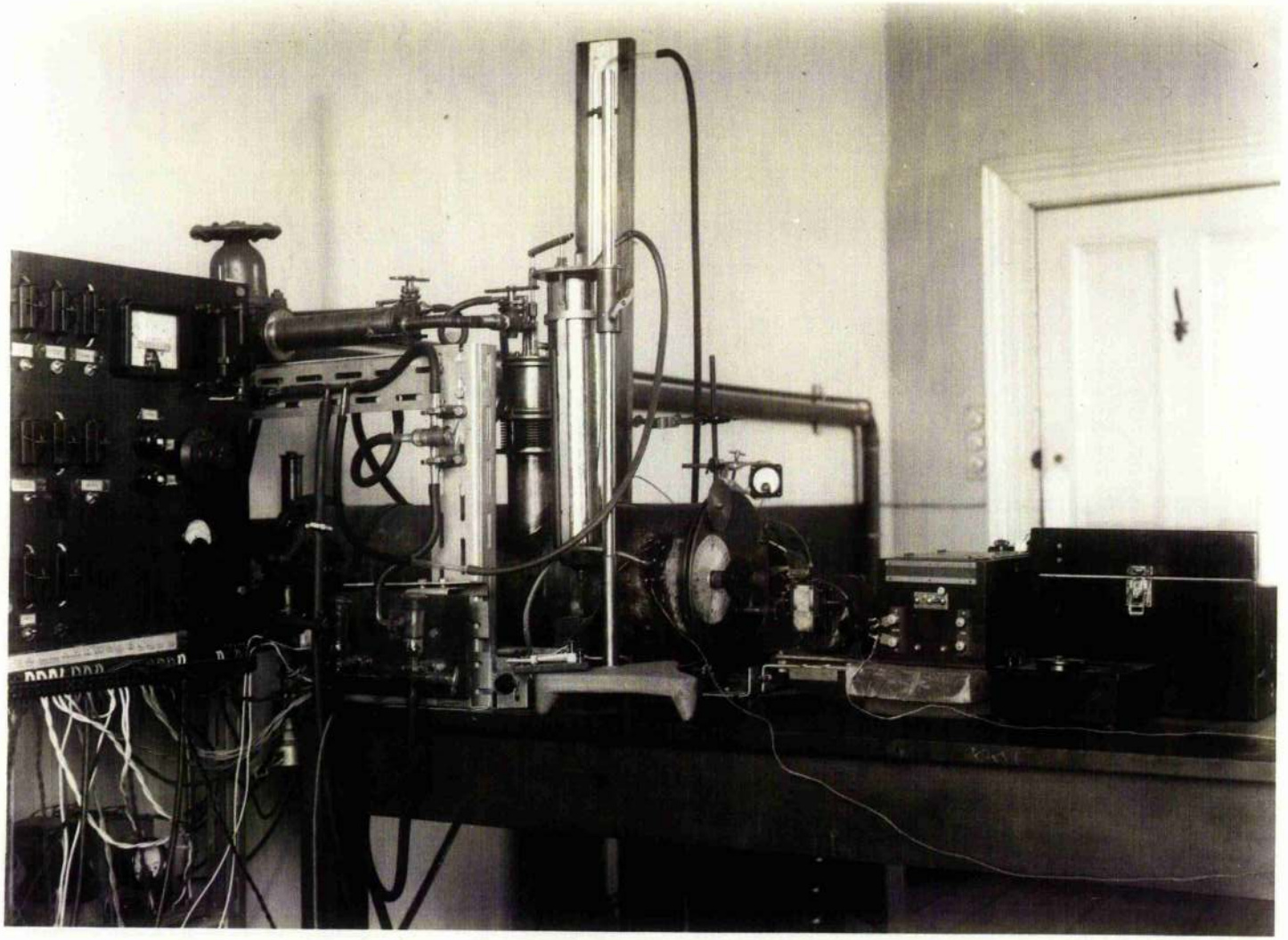


Fig. 3. Vacuum tank with auxiliary apparatus including transfer dewar.

seals and are thus free to rotate, permitting adjustment of the mirror in the system. Further control is available using a sylphon bellows inserted in the supporting tube which enables the whole cryostat system to be tilted. The controlling shutters in the optical system are moved by rotatable rods which are led out through one end plate by a seal consisting of a rubber ring encircling the rod and forced into contact with it by a chamfered brass ring which slips over the rod and is pressed against the ring by a screwed collar.

This type of seal works well when only intermittent rotation of the rod is required but the chopping wheel had to be driven by a driving shaft which, although fairly lightly loaded, was rotated continuously at about 3 revs./sec. It was found undesirable to run an electric motor inside the tank as the varnishes used in most motors have a fairly high vapour pressure even at room temperature and, in addition, even when underrun, the motor gets extremely hot due to the lack of convective cooling. One method of eliminating this difficulty is to use an induction motor in which the rotor has no windings carrying currents. The rotor can be mounted, free to rotate, inside a tube projecting from the vacuum tank. The stator can then be slipped over the tube and the motor will work in the normal way except that the vacuum wall comes between the rotor and the stator. To avoid eddy current losses in the intervening material it must be insulating and, as it must be thin and yet able to stand atmospheric pressure, almost the only available material is glass. This arrangement was tried with several glass tubes but was finally abandoned because the smallness of the gap between the rotor and the stator made it impossible to obtain glass tubing of sufficiently thin wall and accurate bore. The only alternative is to take the rotating shaft out through the vacuum wall

but the normal type of clamped, rubber ring seal is unsatisfactory as the rings give rise to undue friction and wear out rapidly. The type of seal eventually adopted is that illustrated by Strong (Modern Physical Laboratory Practice p. 134 1948). It makes use of a pressure feed of vacuum grease into the bearing and the rotating shaft has a double thread cut in it, one half of the length with a right hand thread and the other left hand so as to provide a pumping action on the grease towards the centre of the bearing and thus prevent its being forced into the evacuated space by atmospheric pressure. A normal clamp seal is also fitted for use when the shaft is stationary.

A T-shaped tube bolted to the rear end plate and sealed by rubber ring supports a liquid air trap and the detector bulb for the Pirani gauge. The tank is evacuated by a rotary backing pump fitted with a phosphorus pentoxide vapour trap and an oil diffusion pump. The diffusion pump is bolted to the stem of a T-shaped vacuum tap, one arm of which is bolted and sealed directly to the side of the tank thus giving the minimum pumping impedance. The tap consists of a flat brass plate which can be forced against a rubber ring mounted on the tank side of the trap thus sealing off that arm. The plate is controlled by a threaded shaft passing through the other arm of the T and is mounted on the end of a sylphon bellows which seals off that arm and eliminates the necessity for packing. All electrical leads are taken into the tank through "covar" metal to glass seals soldered through the tank wall. Possibly because of the large mass of metal to which they were soldered involving intense heating during soldering many of these developed cracks while in service.

The pressure inside the tank was measured by a Pirani gauge. The detector was constructed from an old pattern of electric light bulb which

has a straight tungsten filament and on to which was sealed a glass tube enabling it to be mounted in the vacuum system using the normal ring seal. These bulbs have a resistance of about 20 ohms and its change in resistance with temperature depending on the pressure of the air is measured using a Wheatstone bridge of which the bulb forms one arm. The power supply for this consists of a 12 v. transformer with a rectifying and smoothing circuit and the current was fed to the bridge through a potentiometer and voltmeter. To eliminate errors arising from changes in the mains supply, the voltage supplied to the bridge was set to a predetermined value before each setting or reading. The bridge was balanced at atmospheric pressure before each run using a rheostat in a balancing arm and the readings of the out-of-balance current measured on a milliammeter taken as a measure of the pressure of the gas. Currents of the order of 50 ma. were obtained as a limiting value when the pressure became too low for the gauge to respond further and, although this was the only significant reading as it indicated that the vacuum was satisfactory for thermal insulation at 10^{-4}mm. of mercury, the gauge was calibrated over the range from 1 mm. to 10^{-4}mm. pressure of mercury using a McLeod gauge. Although the filament was not outgassed before use, the final readings indicating a thermal vacuum were consistent to about 2%. Any variation inside this range of error was presumably the result of ambient temperature changes occurring in the room since the bridge was balanced as no compensating filament was included.

Because of the large volume of the vacuum space and the large amount of metal with soldered joints and other undesirable features like electrical insulation inside the tank the pumping speed down from atmospheric pressure was low but, once evacuated over a period of a day or so, and well outgassed, the rise of pressure after pumping stopped was not

serious and, even after standing for a few days, the apparatus could be re-evacuated to a thermal vacuum in 20 minutes. Leaks were detected by covering suspected areas with shellac varnish while the tank was evacuated and the Pirani gauge in operation. The drop in pressure as the leak was covered was not so abrupt as it is in a small system but the shellac usually effected a permanent seal in addition to detecting the leak. The worst offenders were the sylphon bellows carrying the cryostats and they were, in consequence, moved as little as possible.

2) Optical System

As the optical system had to be removable from the vacuum tank to allow of adjustment outside and the apparatus is very sensitive to alterations in alignment, it had to be mounted very rigidly (fig. 4). The important part of the system is that following the beam splitting mirror and the support for this section is a solid brass plate 1/4" thick. All the mirrors are carried on pillars bolted through holes in the plate and the shutters, which are very important, were mounted very rigidly on the diaphragm which is well braced and bolted to the base plate. The collimating system is not quite so critical and it is carried on two girders which act as extensions of the base plate.

Since the first requirement in the work was in the infra-red, the choice of the most suitable type of source had to be considered. Wave-lengths as far into the infra-red as possible were desired and normal thermal sources are unsuitable because of the very low intensities of long wave-lengths even at high temperatures. Easily the best source for wave-lengths of 100 μ and upwards is the high pressure mercury arc which was shown by Rubens and Baeyer (1911) to emit wave-lenghts ranging up to 300 μ. This radiation seems to be the result of a resonance band in the mercury

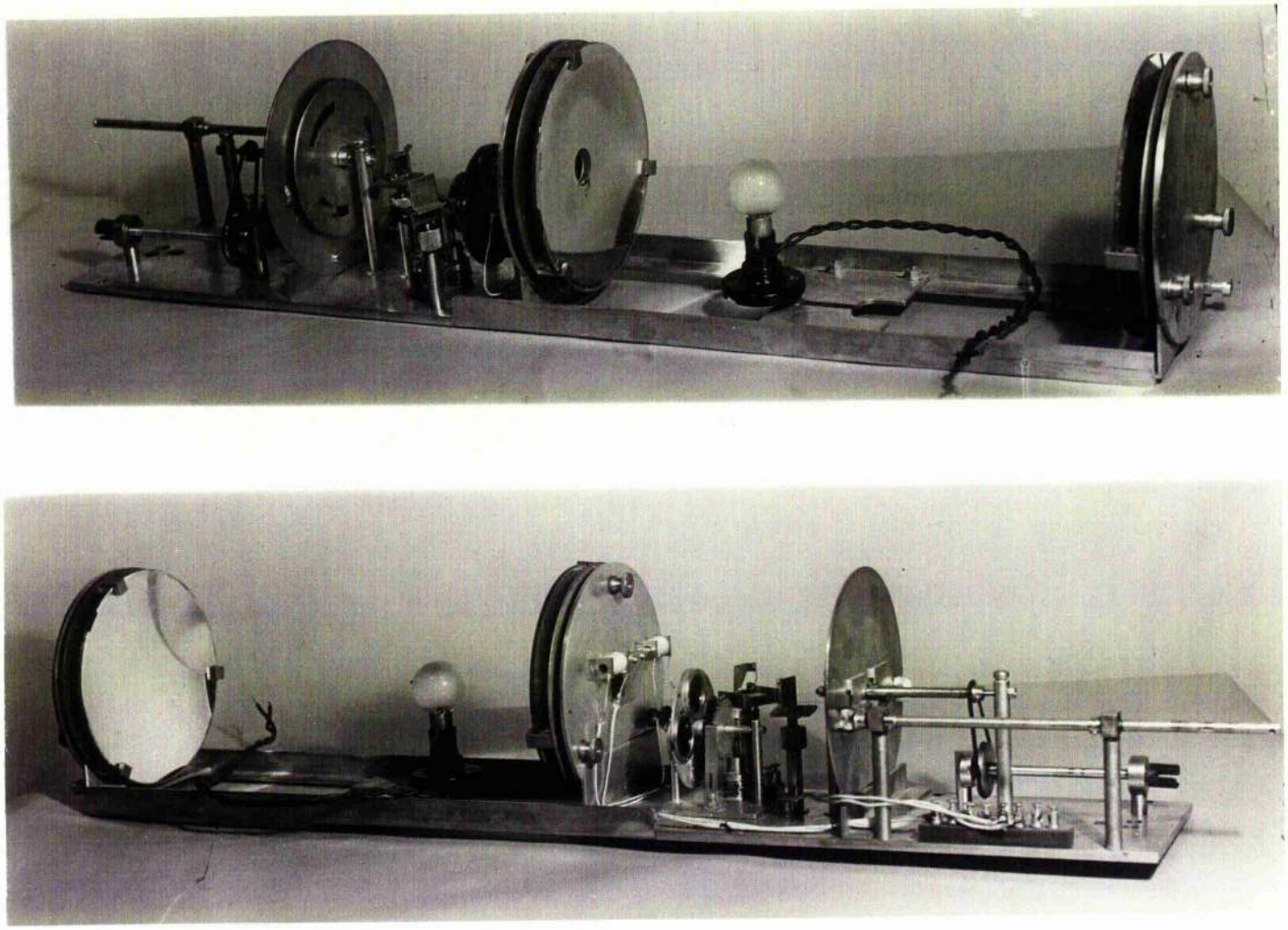


Fig. 4. Optical bench .

spectrum giving greatly enhanced emissivity. It is produced to the greatest extent by high pressure arcs running at high current densities and is quenched by any auxiliary carrier gas. These long wave-lengths rays are transmitted well by natural quartz and to a rather less extent by fused quartz, paraffin and black paper. In the middle and near infra-red regions orthodox sources are superior and in the visible there is no problem.

The sources actually used were two mercury arcs and a car headlamp bulb. The mercury lamps were the type MA 80 watt Osram lamp and the type ME 250 watt Mazda lamp. Both are high pressure lamps in quartz bulbs and have no carrier gas other than the mercury vapour so that they satisfy all the conditions for the production of the very long wave-length radiation. The Osram lamp gave reasonably steady emission but proved too wide and diffuse a source. The Mazda lamp was much superior in this respect since it provides an extremely intense arc only a few millimetres long but suffered from the very serious drawback of random arc movement. The arc takes the form of a curved filament bowed out to one side of the electrodes and when this filament moves round the electrodes it results in a displacement of the source by about 1/2 cm. In any double beam system the distribution of the light between the two parts of the split beam is of the utmost importance since it is essential that this remain constant during an experiment. Attempts were made to stabilise the arc using a magnet but it was found that if too strong a field were used, the arc was blown out and if a weaker field were used it was not strong enough to stabilise the arc completely. Mercury lamps also give trouble when a.c. detecting methods are used because of the high level of random noise superimposed on the emission although this is not too serious when a narrow band-pass detecting system is used. Probably the most suitable source would be a

capillary arc with a well regulated voltage supply. The existence of emission from the lamps which could pass through photographic black paper, which is recommended by Rubens and Baeyer as a filter, was verified using a normal type of thermopile and galvanometer. It was checked that this stopped immediately the lamp was switched off showing that the radiation originated in the mercury vapour and not in the walls of the lamp.

In the visible and near infra-red the most suitable source was found to be an 80 watt car headlamp bulb. This was stable and noise-free and gave ample intensity of emission with a reasonably small size of source. Most of the results to be presented were obtained using the incandescent sources but some figures from earlier runs using mercury arcs are included.

The power supply for all the lamps consists of a 230 v. rectifier to produce a direct current which is smoothed by four 10 henry chokes in parallel connected in series with the lamp and by a 44 μf condenser across it. This arrangement of the smoothing circuit proved to be the most effective for providing a stabilising influence on the mercury lamps. A rheostat and ammeter were included in the circuit for intensity control.

Once the source of the radiation has been chosen some method of isolating a reasonably narrow range of wave-lengths is required. No strongly wave-length dependant features in the reflectivity were expected so that, in the visible at least, it was regarded as adequate to obtain the desired wave-lengths by filtering the light emerging from the collimator. In the visible and near infra-red the filters used were 1" diameter, glass enclosed gelatine discs numbers 602, 604, 606, 608 and 207 supplied by Ilford. These have maximum transparencies at wave-lengths of .47μ, .5225μ, .59μ, .68μ and about .93μ respectively with a band pass for those in the visible of about .02μ and about .2μ for the infra-

red one. These filters are mounted just outside the collimator on a brass disc (fig. 5) which can be rotated so as to bring each filter in turn into the light beam. The shaft on which the disc is mounted can be rotated by a ratchet and pawl system which is activated by a solenoid with a controlling switch outside the tank. This allows the filter to be changed while the tank is evacuated permitting measurements to be made on more than one wave-length during one run and also facilitates the measurement of the wave-length variation of the specimen's reflectivity by enabling the filter to be changed without altering any of the other settings in the optical system.

This gives directly only the wave-length variation of the specimen compared with that of the reference mirror and so, in order to obtain absolute results, the latter must be determined in a separate experiment and used to correct all the direct measurements. This determination need be made only at one temperature as the reference mirror remains at room temperature during the experiments. The surface of the reference mirror was aluminium which has a very low wave-length variation of reflectivity in the visible so that the above correction was small.

In the infra-red it is not easy to obtain a narrow band of wave-lengths using filters and other standard methods such as these using prisms or gratings are cumbersome and unsuited to the present purpose. The method using multiple reflections from halide crystals to yield reststrahlen is reasonably convenient and adaptable but imposes a restriction on the wave-length to those available from the crystals in common use. The method by which the very long infra-red wave-lengths were first isolated by Rubens and Wood (1911), that of focal isolation, is simple and convenient. The system consists simply of a quartz lens and use is made of the high dispersive power of quartz to focus and concentrate the long rays for which the refractive index of quartz is near its limiting value of 2.14 while the shorter wave-lengths,

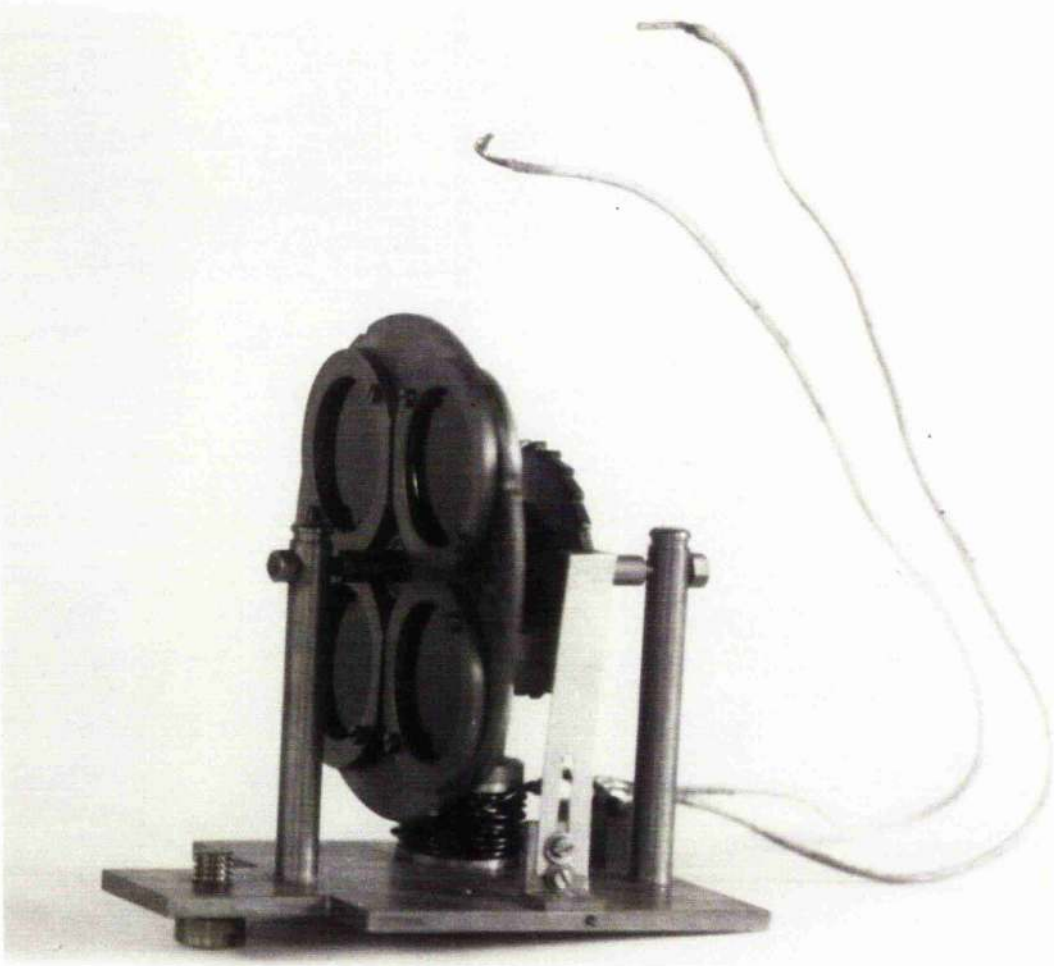


Fig. 5. Filter holder.

for which the refractive index is much less, actually diverge on passing through the lens. However, like the reststrahlen method, the wave-length adaptability is poor and the large quartz lenses which are required are difficult to make and expensive. The very long waves seem to present less of a problem than the intermediate region as it is claimed that ordinary photographic black paper acts as the most efficient filter. It is quite transparent for the longest rays but cuts off completely those shorter than about 100/. Thus as a result of the objections outlined above to all other methods, it was felt that, for the present purpose, filtering offered the best and most convenient method of wave-length isolation throughout the whole spectrum.

Since no complicated wave-length isolating systems were involved, the collimator was thus required merely to produce a concentrated, parallel beam of radiation. Because of the necessity of covering a large wave-length range, mirrors were used throughout in the optical system. The condenser consists of two spherical mirrors 6" in diameter and of 6" focal length (see fig. 1). The source is placed at the prime focus of one and the emergent parallel beam is brought to a conjugate focus by the other. Light from this is collected and collimated by the small spherical mirror. The function of the large mirrors is merely to provide a transparent source as the solid angle collected remains constant through the system. The extent of collimation provided by the small mirror which is only $\frac{3}{4}$" diameter is limited by the size of the source but was normally adequate as the area of the beam is limited later in the system in the interests of homogeneity. The collimated beam then emerges through a $\frac{3}{4}$" diameter hole trepanned out of the centre of the mirror M_2. The big mirrors are mounted on three screws tapped through a brass backing plate so that they can be tilted to align the beam. The small spherical mirror, like all the other small mirrors can be rotated about all three axes and both this mirror and the source are mounted on a bridge between the two girders.

This has slots in which the mirror and source can be moved along the axis of the system to permit accurate focussing. The space occupied by this part of the system is sufficiently large to allow of the substitution of another form of wave-length isolation like the reststrahlen or focal isolation methods if required. All the mirrors in the system are of aluminium-fronted glass.

The aperture which allows the radiation to leave the collimator can be closed by a brass shutter suspended from a soft iron rod which slides horizontally through two solenoids so that it can be pulled to one side or the other to open or close the shutter. The filter holder is mounted immediately outside the collimator and the beam passes to the splitting mirror. This can be rotated as a whole and the angle between the two parts varied so that complete control over the distribution of the light between the specimen and the reference mirror is possible. The chopping wheel which follows, is a brass disc with three rectangular-ended slots cut out so as to pass the beams alternately. It is carried on a shaft driven through pulleys by a driving shaft mounted lower on the base plate. This, in turn, is rotated through the vacuum seal by a universal joint just inside the tank. The universal joint corrects for any lack of alignment between the driving shaft and the shaft in the seal and, as the two parts of the joint are simply pushed together, allows the end plate to be removed without having to pull the shaft out from the seal.

The driving motor is a 110 v.d.c., shunt wound motor coupled to the seal shaft by gears and mounted on rails so that it can be moved back to allow the tank end plate to be removed. The rectifier for its power supply is fed by a variac to provide speed control with fine control using a variable resistance in the field coil circuit. The speed stability of the motor must be reasonably good to keep the chopping frequency constant for, since the amplifier is tuned to one frequency, loss in gain with consequently reduced

sensitivity will result from change in chopping frequency. This is inconvenient but, because of the mil nature of the measurements, not critical and the stability of the motor proved adequate. Its main drawback was in the production of noise due to sparking at the commutator brushes which was transmitted through the mains supply to the amplifier and detector circuits. This could be remedied by readjusting the brushes and was minimised by altering the gear and pulley ratios so as to run the motor as slowly as possible.

The screen following the chopping wheel has two apertures to limit the area of the transmitted beams and carries the shutters controlling the beam intensities. The shutters are mounted on screws so that they can be traversed across the apertures and the screwed shafts are rotated, through bevel gears, by the control shafts which are led out through the tank end plate. About 10 revolutions of the shaft are required fully to close one shutter and the amount by which the shutter in the specimen beam has been moved is measured by a counting disc moved one space at a time by the pointer on the control rod for whole revolutions and a 360° protractor for parts of a revolution. The shaft for the reference beam shutter was not normally mounted and the shutter setting was adjusted by hand before an experiment to avoid the possibility of this shutter being moved while measurements were being made.

3) Detecting and Amplifying Systems

The requirements of the detectors included not only sensitivity but also the ability to respond to alternating light signals. In the case of electronic detectors like photocells this presents no problem but it is much more difficult for infra-red detectors and the chopping frequency was, on that account, limited to 15 c/s.

In the visible region of the spectrum the detector used most was the General Electric type 931A electron multiplier photocell. These cells, which have been fully described by Engstrom (1947), have the advantage of the extremely

high sensitivity resulting from the nine stage photoelectric amplification. The signal is taken from the anode load resistor and coupled into the first stage of the amplifier using an RC filter. For convenience in extracting the signal the positive side of the high tension is earthed and the cathode is run at a suitable negative potential. Although these cells were underrun at about 50 v. per stage, it was found that each one used became noisy after a period of use extending up to six months. The d.c. characteristics remained unaltered but the cell became useless for sensitive a.c. work. In spite of this, almost all the work on the visible region was done using a photomultiplier. The normal disadvantages of these cells, the rapid dependence of anode current on anode potential and the variation in sensitivity over the area of the cathode were not important from the nul nature of the measurements and the fact that only changes in reflectivity were being measured.

To cover the intermediate range between the visible and the infra-red, a Cintel size 600 photocell was used with an S type cathode. This cathode has a lower sensitivity over the visible range than most other cathodes but it remains sensitive into the infra-red up to 1.2 μ with a peak at about 0.8 μ. The cells used were gas filled which was unfortunate because of the higher instability compared with vacuum cells but was necessary on account of the low absolute sensitivity of the cathodes.

The photocells were mounted so as to receive the two beams directly on to their cathodes without further focussing. They were therefore mounted horizontally, the base being carried on a vertical metal support which could be clamped to the baseplate of the optical system and adjusted to ensure that both beams fell within the cathode area. The high tension supply for the photocells was provided by a normal power pack with a full-wave valve rectifier and two stage choke-capacity smoothing. It provides about 500 v. and is supplied to the photocells through a potentiometer.

The detectors used in the infra-red included a Hilger-Schwartz linear thermopile type F 1407 with a sensitivity of 5μv/μw. and a response time of about 1/50 sec. It is contained in a small cylindrical shield which was supported on a pillar for mounting on the base plate and the radiation was focussed on the receivers using the small sherical mirrors. As the impedance of the thermopile is very low the output from it was fed to the amplifier using an input transformer with an 80 : 1 step-up ratio which was designed and supplied by Partridge. Grid bias for the first valve of the amplifier was provided by a 2 v. accumulator in series with the secondary winding of the transformer. The main difficulty in this arrangement was found to be 50 c/s. pick-up from the mains which, despite the careful shielding of the input leads, the enclosure of the transformer itself in a metal case and the low response of the amplifier to this frequency was sufficient to make the use of the thermopile very difficult.

On this account the second detector was the more suitable for use in an a.c. system. This was a thermistor bolometer made by Bell Telephone Labortatories and supplied by Dr. G.E.Hyde of the United States Scientific Commission in the United Kingdon. The Bell thermistors have been described by Becker and Moore (1946) and Bratten and Becker (1946). They make use of thin flakes of a semiconducting material with a large temperature coefficient of resistivity which are mounted on a quartz block which serves as a heat sink. Although in the present case the detector took the form of a bridge network with two thermistor flakes and two balancing arms, by far the more sensitive arrangement for a.c.work is a simple series circuit like a photocell circuit where the signal is the change in potential across a resistor in series with the sensitive element. These bolometers become noisy with age but this is outweighed by their high resistance of about 5MΩper arm and general adaptability to a.c. methods. The high tension supply for the bridge was the power pack already described and the potential applied was controlled so that

the total current flowing in the circuit did not exceed 30 μa. Because of the fact that the signal from the bridge was developed across two corners of the bridge instead of between some live point and earth, it was found that the most convenient way of coupling the detector to the amplifier was through a push-pull in-put stage with the grids connected directly to the corners of the bridge and the cathode tapped along the supply voltage to ensure that the grid bias was correct. A variable cathode resistor then enabled the system to be balanced to compensate for any lack of balance of the bolometer bridge at the working temperature. The output from this stage was coupled to the main amplifier using a push-pull output transformer.

The amplifier itself (fig. 6) was required to amplify only a very narrow band of frequencies as times involved in alteration of the signal amplitude were long compared with the period of the signal. The first amplifier built was copied directly from Roess (1945). This is a push-pull amplifier designed to detect very small signals at a fixed frequency, the tuning being achieved by twin-T resistance-capacity feedback networks. It was designed for use with a radiation thermopile only and, on account of the consequent lack of adaptability and instability under other conditions, it was abandoned for the present work. Since a narrow band pass is essential to eliminate hum and other noise the method finally adopted to obtain the required selectivity was straightforward tuning using a parallel L-c circuit with a Varley choke of about 3,000 henrys and a 4 μF condenser. This provided a working frequency of about 12 c/s. The Q value of the circuit is obviously low but the effective limits of response (gain down to about 10% of the peak value) are about 8 c/s and 20 c/s which eliminates practically all spurious signals.

The first stage of the amplifier has a 6J7 pentode with the tuning circuit in its anode circuit. Precautions are taken to reduce noise, hum pick-up and microphonics by mounting the chassis on foam rubber supports and

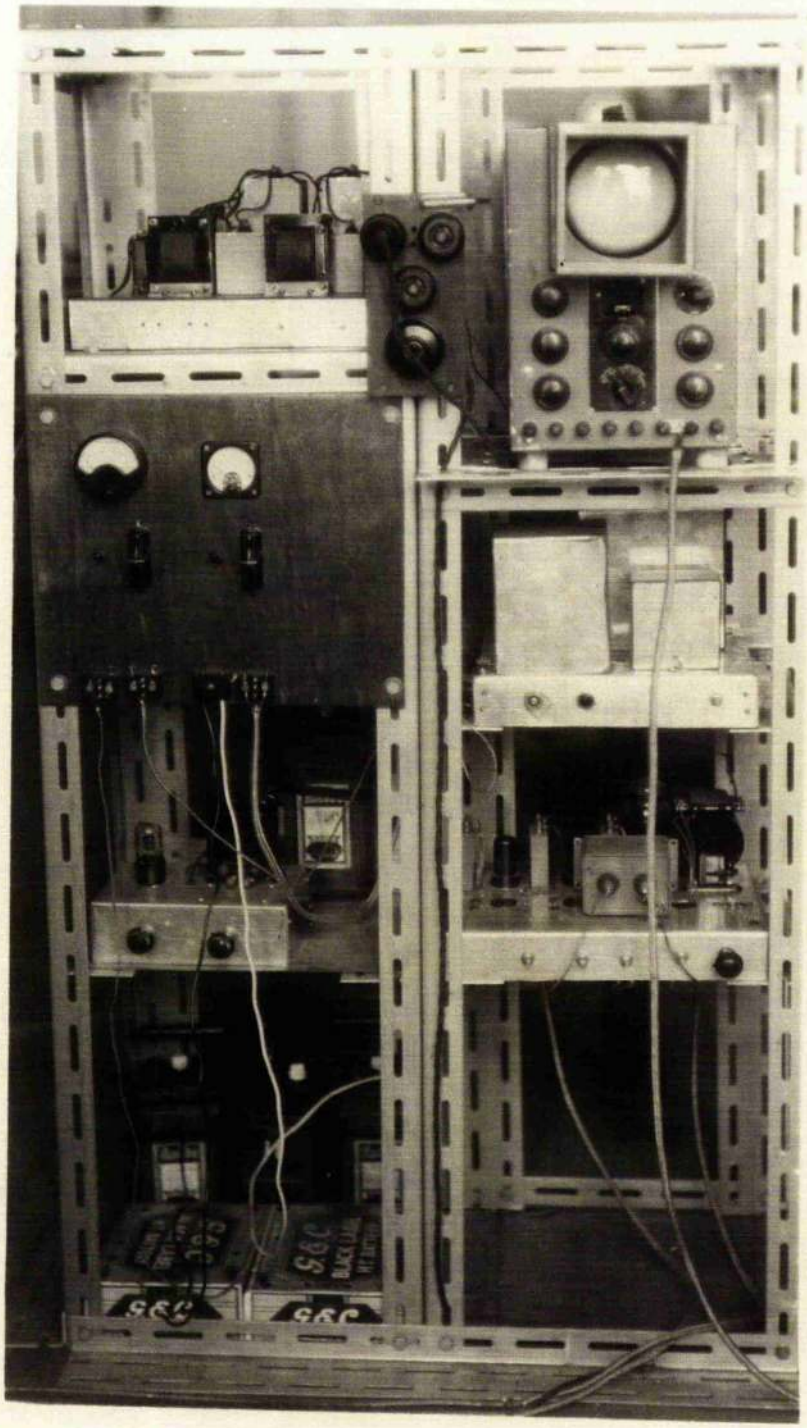


Fig. 6. Amplifiers. The components on the right are the pre-amplifier and the main amplifier. On the left are the output filters and the push-pull pre-amplifier.

using batteries for the cathode heater and high tension supplies. All components are protected against electrostatic and, as far as possible, electromagnetic, pick-up by enclosing the valve chokes and transformers in metal cans. The main amplifier is a normal, three stage, R-C coupled amplifier with two pentode stages using 6AC7's and a low impedance output stage with a 6L6. The high frequency responce is limited using a .01 µF condenser as a short circuit to earth from the anode of the first pentode and stability is improved by negative feedback applied from the anode to the grid of the second pentode stage. The amplified signal is taken from the output valve by a transformer with a very high primary impedance and passes through a low pass π-section, L-C filter with a cut-off between 20 and 30 c/s to remove noise and hum. It is then rectified by a full wave selenium meter rectifier and the ripple is removed using a normal L-C smoothing circuit. The meter used to detect the signal and thus make the balance settings is either a Unipivot 120 µa centre zero meter or a Tinsley box galvanometer with a sensitivity of 25 mm/µa when greater sensitivity is required. The amplifier is sufficiently stable that, even when the galvanometer is used, the deflections are so steady that a magnifying lens can be used in front of the scale enabling deflections of 1/10 mm. to be detected. The output signal at the anode of the last valve can be monitored by a cathode ray oscilloscope, and the sensitivity of the system can be controlled by a normal gain control in the grid circuit of one of the pentodes and a potentiometer across the final smoothing stage from which the signal is supplied to the meter. The total voltage gain of the amplifier is about 6.10^5 and the noise characteristics such that, with zero signal applied to the photocell, the current on the output meter is less than 1/10 µa.

An attempt was made to use an electron multiplier photocell as an amplifier. The principle is that, since the multiplier acts as a current amplifier, any fluctuation in the current in the first stage will appear at the

final anode amplified to the same extent as the current itself. Since this amplification is of the order of 10^6 in good cells, comparable voltage amplification ought to be possible. Such an arrangement was tried with the signal applied in series with the accelerating potential applied to the first stage between the cathode and the first anode. Either transformer or RC coupling was used to obtain the amplified signal and voltage gains of up to 100 were found depending on the intensity of the light used to activate the cell. The reason that this is so much lower than the expected value is that superimposition of the signal on the first anode potential is such an inefficient way of modulating the electron stream as the effect depends on the ratio of the signal voltage to the stage potential of about 50 v. If a control grid were used between the cathode and the first anode much more efficient modulation could be achieved and high amplification obtained. This would result in an amplifier which was compact and simple and, although subject to the fairly high noise level to which electron multipliers are prone at high frequencies, would have many advantages over normal amplifiers in many ways such as frequency response. It would, however, be of limited application as it could deal with very low input signals only so as to avoid saturation of the later stages.

The power unit for the main amplifier is a normal double diode rectifying and smoothing unit with a stabilizing stage. This is of the common d.c. amplifier type where the high tension current is controlled using a low resistance triode as variable series resistance. The output voltage measured across part of a bleeder resistance is compared with that across a neon stabilising tube by applying one to the cathode and one to the grid of a high gain pentode. The output from this is applied to the grid of the controlling triode thus compensating for any change in output voltage of the rectifying unit by altering the resistance of the triode.

The amplifier units are mounted on a metal framework at one side of

the apparatus while all the other electrical apparatus is mounted on another rack at the other side. The power units are mounted on the latter rack so as to avoid 50 c/s pick-up in the amplifiers and most of the electrical equipment is supplied from a saturated core stabilising transformer which is kept even further away on account of its very strong magnetic fields.

4) Cryostats

Since the whole apparatus, in effect, constituted the cryostat, we are concerned only with the actual liquid gas holders which supported and cooled the mirror. The first type of cryostat (figs 7 & 8) which was used only with liquid air consists simply of a german silver tube about 1" diameter and 8" long which projects through, and is supported by, a flanged brass plate resting, as described before, on a rubber ring seal on the main apparatus. The tube is open at the top and is closed at the bottom by a copper block which acts as a mirror holder and is recessed so as to allow the face of the mirror to lie on the axis of the tube. Two holes drilled in the block allow the liquid air to circulate inside it and the mirrors can be soldered to the face of the block or clamped to it by a screwed collar. A thermocouple could be clamped behind the specimen or soldered to the block and the leads taken out through cover seals in the supporting plate. This cryostat held a mirror $\frac{3}{4}$" in diameter and $\frac{1}{2}$" thick and early experiments down to liquid air temperatures were done using it. It was, however, found that a simple clamp fit did not, apparently, provide sufficiently good thermal contact between the liquid in the cryostat and the mirror. As the mirror is almost entirely surrounded by surfaces at room temperature, the radiation heat influx was sufficient to give quite a few degrees temperature difference across the poor thermal contact obtained by clamping. Any later experiments using this cryostat were done by soldering the mirror to the block with Wood's metal and no further difficulty about temperature gradients was experienced. The good absolute reflectivity

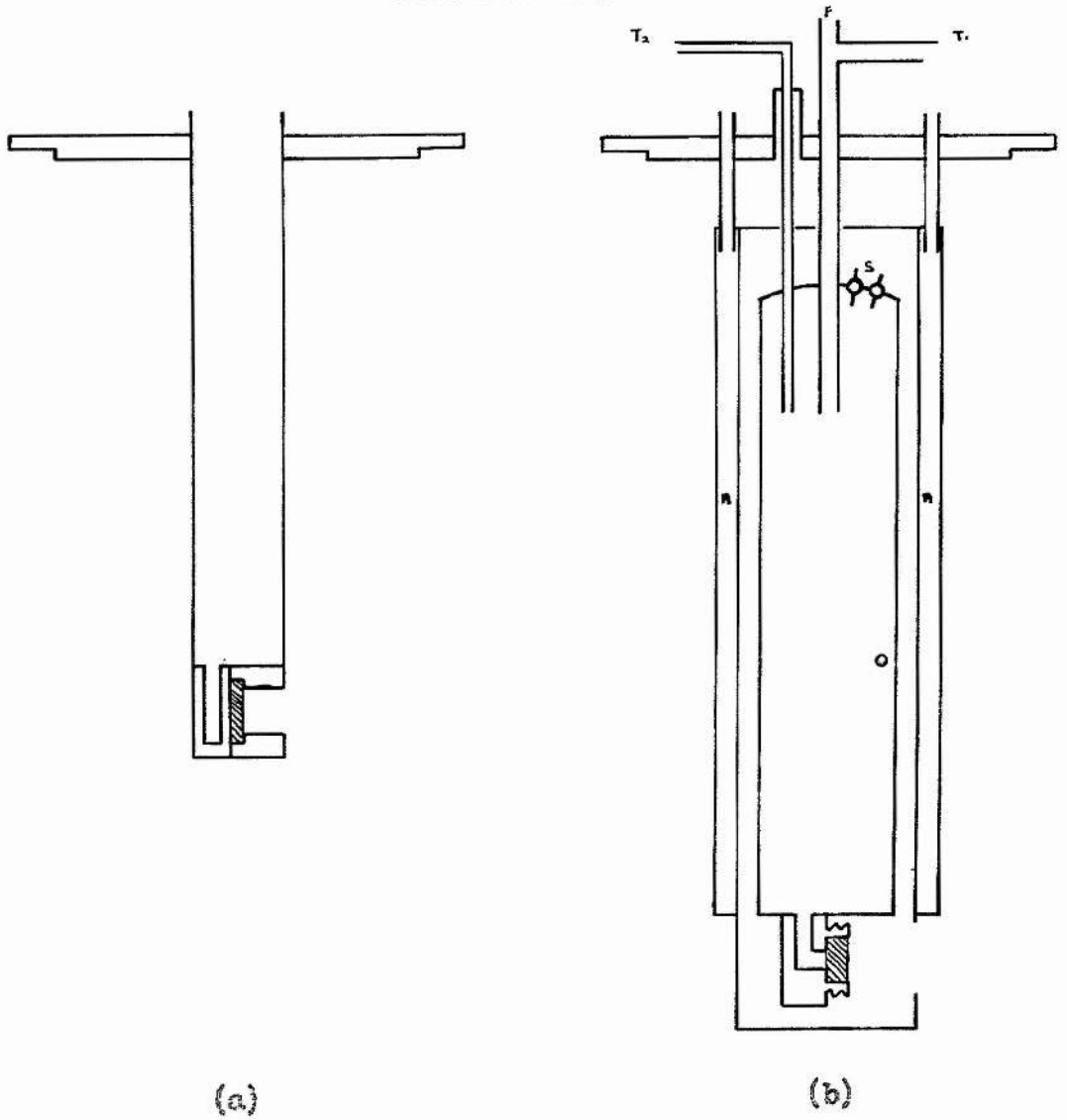


Fig. 7. (a) Liquid air cryostat. (b) Liquid helium cryostat. The mirrors are shaded.

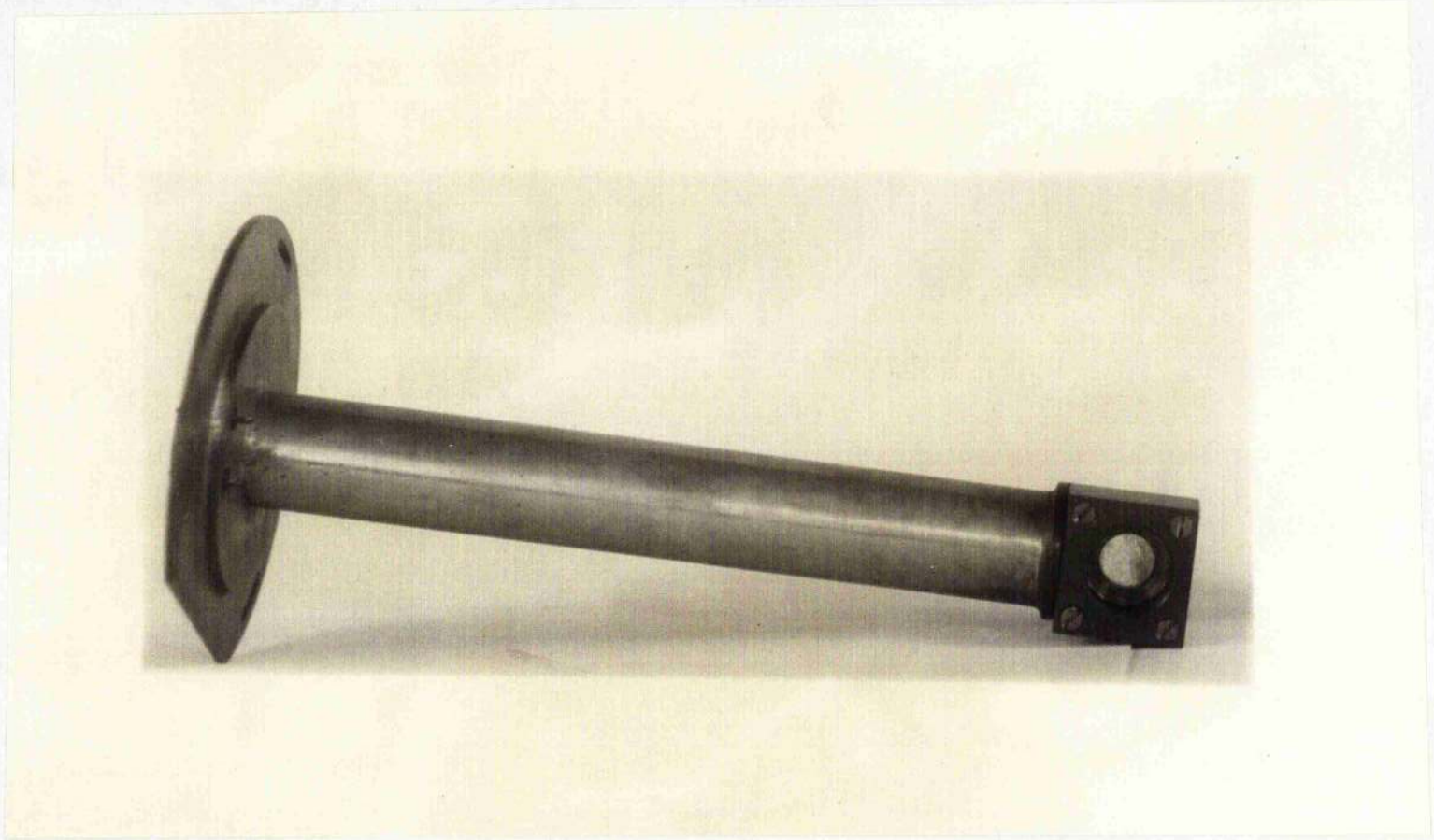


Fig. 8. Liquid air cryostat.

of the specimen ensured that, once good thermal contact with the bath had been achieved, the temperature difference due to irradiation of the surface by the measuring beam between the surface and the back of the mirror where the temperature was measured was less than .01%.

The second type of cryostat (figs 7 & 9) was designed for use with liquid hydrogen and helium and a mirror ½" in diameter and 1/16" - 1/8" thick and is similiar in principle to the pattern described above. It differed in that, to reduce the heat leak to the cryostat, the actual liquid helium container is suspended from the supporting disc by a thin-walled german silver filling tube. The liquid helium container is a german silver tube as before but of larger diameter than the early one and it is closed at the top by a spun copper disc through which the filling tube and the blow-off tube were soldered. The mirror holder consisted of a small copper block soldered to the plate closing the bottom of the cryostat and more efficient cooling was achieved by leading the coolant through ducts drilled in the block right to the back of the mirror which was soldered to the holder with Wood's metal.

Before the technique of soldering the mirror to the holder was adopted and the mirror was merely clamped in place, some kind of vacuum seal had to be used between the holder and the back of the mirror. This seal had to be effective with a pressure of 10^{-4} mm. of mercury on one side and liquid air or hydrogen on the other. Under these conditions rubber seals are quite useless and a gold ring seal supplied by Ferranti Ltd. of Edinburgh were tried. These were found to give excellent results when used between carefully aligned brass plates which had been accurately machined to a plane surface. They were, however, found to be unsuited to the present purpose because of their inconvenience. The seal is extremely sensitive to the distribution of pressure round the circumference of the ring since the wire of which it is formed is less than ½mm. in diameter. Furthermore, when used with a metal such as tin which is softer

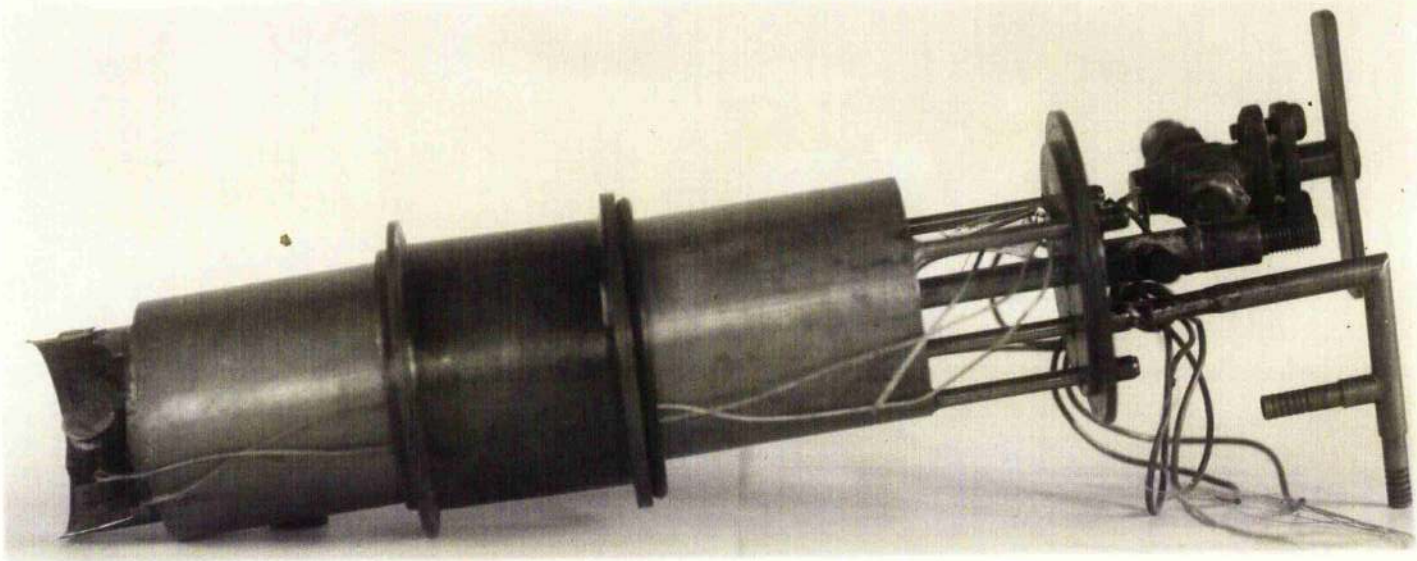


Fig. 9. Liquid helium cryostat. The cylinder encircling the liquid air jacket is the spacer forming part of the cryostat support in the vacuum tank.

than gold, a permanent circular groove is formed in the face of the metal at the pressures required to give a satisfactory seal and this made a re-seal with the same specimen virtually impossible.

The thermocouple for temperature measurement was soldered to the back of the mirror and the leads taken through the bath to reduce the heat leak to the mirror and out at the top of the cryostat. The filling tube ends above the supporting cap in a union to fit the liquid hydrogen and helium filling tubes and has a side tube through which the thermocouple wires are taken out through a gas-tight seal. It then leads through a tap and a demountable seal, fitted with a sylphon bellows to take up any lack of alignment, to the main pumping line which terminates in a Saunders packless valve. The second tube from the top of the cryostat, which serves to remove the gas evaporated in cooling the cryostat, which serves to remove the gas evaporated in cooling the cryostat and to maintain a vapour pressure of one atmosphere for measurements at the normal boiling temperatures of liquid hydrogen or helium, is taken out through the cap by a length of vacuum jacket to minimise frosting of the cap and then via a tap to the atmospheric pressure return line to the gas holder. A side tube from this line allows a manometer to be inserted for measurements of the static pressure over the liquid gas while it is being pumped. The gas handling system described above is that designed for use with liquid helium and uses a large Pulsometer pump. A second system duplicates this on a smaller scale using a small Hyvac pump for use with liquid hydrogen. A T-shaped selector tap allows the hydrogen gas either to return to the gas holder at atmospheric pressure or to be pumped to reduce the temperature.

Temperatures were measured using a copper-constantan thermocouple with a silver soldered junctions and the reference junction in a small dewal vessel containing an ice-water mixture. The emf of the thermocouple was measured using a Doran direct reading potentiometer which has a sensitivity of

.03 mv./cm. and temperatures could thus be read (ideally) to .04° K although this accuracy was never used. The thermocouple was calibrated at one temperature using liquid oxygen. This calibration reading then enabled a proportional correction to be applied to the values given by Landolt Bornstein and for the emf. of a copper-contantan thermocouple at various temperatures and this curve was then extrapolated to liquid hydrogen temperatures using a divided difference table.

A level indicator for liquid helium is provided by a tantalum wire mounted vertically in the cryostat. Tantalum is a super-conductor with a transition temperature of 4.38° K so that, when partially immersed in liquid helium, the junction between the normal and superconducting parts of the wire should not be far above the surface of the liquid helium and the total resistance of the wire will give a measure of the liquid helium level.

The thermal properties of the cryostat were sufficiently good that one filling of perhaps 600 cc. of liquid hydrogen would cool the cryostat and then last for about 4 hours. The heating rate after all the hydrogen had evaporated was about 1°/min. at the beginning of heating. This heating rate could be accelerated, when desired, using a small heater of constantan wire wound round the mirror holder and fed by two 2 v. accumulators through a controlling resistance and ammeter outside the apparatus.

Chapter 5

All the theory given earlier assumes that the metal surface is plane and that the properties of the metal within the depth of penetration of the radiation fields are essentially those of the bulk material. Consequently, in experiments on reflecting power performed with the aim of obtaining information applicable to the bulk metal, great care must be taken in the preparation of the surfaces so as to satisfy these conditions. The first requirement, that of planeness, is not too serious if only the temperature or wave-length variation of reflectivity is required and not absolute values. It is therefore justifiable to sacrifice fine finish of the surface if the production of that finish is going to involve any other difficulty.

The second point is much more important. The early experimenters had assumed that, provided their surfaces were polished so as to show a reasonable amount of specular reflection, the precise nature of the surface was not important and it was not until the work of Beilby (Aggregation and Flow in Solids) that a detailed investigation of the mechanism of polishing was undertaken. It is obvious that any process which removes metal in an attempt to secure a plane surface is going to strain the material to a certain extent and it has long been known that the grinding action of carborundum or other abrasives on hard, brittle materials like glass or speculum metal was the result of "conchoidal" fracture which cracks off flakes of the material. This presumably leaves the surface strained to a certain extent but it is not likely to distort the crystal structure very much. However, Beilby suggested that the mechanism of polishing with fine polishing agents like rouge or alumina was completely different and due to plastic flow of material over the surface. By microscopic examination of a scratched metal surface at various stages of a polishing process he was able to watch the growth of a surface skin which was caused to flow over the scratches and other imperfections to form, eventually, a completely polished surface. He observed that the surface can be caused to

flow in this manner only by the use of the finest polishing agents like rouge which seemed to have the property of adhering to the surface as a whole and that the polishing of even the hardest and most brittle materials, such as glasses, is the result of plastic deformation. The mechanical and electrical properties of such a highly cold worked material as this film can be expected to be quite different from those of the undistorted bulk material and this was verified by Beilby in certain cases such as hardness and resistance to acid attack. The effect on the optical properties of a metal could be considerable as the thickness of the distorted layer may be as much as 10^{-4} c.m. which would mean that the whole penetration depth of the radiation would be contained in cold worked material and the optical properties would be governed by the resistivity of highly abnormal material.

The conclusions of Beilby were almost immediately supported by evidence from other methods of examining the surface. Many electron diffraction experiments were done by G.P. Thomson (1920) and others (Finch, Quarrel and Roebuck 1934, French 1933, Darbyshire and Dixit 1933) who showed that the surface of a highly polished metal is, indeed, amorphous. The effect on the reflecting power directly was shown by Lowery and Moore (1932) and Lowery, Wilkinson and Smare (1936) who investigated the effect on the absolute reflecting power of the method of preparation of the surface. They used different grinding and mechanical polishing methods and, for the first time in optical work, electrolytic polishing and showed that the reflectivity of a lightly polished or electrolytically polished surface is about 10% higher than that of a heavily burnished surface.

The effect of temperature on the resistivity of this highly worked layer which is determining the reflectivity is not so easy to predict. It could be argued, eg. as by Mott and Zener (1934), that the residual resistance of such a layer would be so high that it would mask the temperature dependent part and a

reflectivity almost independent of temperature would be predicted. Moving away from this extreme, a more and more nearly normal temperature variation would be expected as the residual resistance became a smaller proportion of the whole resistance and if the effect on the absolute reflectivity is only 10% the complete quenching of the temperature variation is not to be expected.

It was with these considerations in mind that the three methods of surface preparation for the three metals studied, silver, copper and tin using electrolytic polishing, casting and annealing were chosen.

1) Electrolytic Polishing.

The phenomenon of electrolytic polishing was first noticed by Jacquet (1936). In studying anodic etching of copper in orthophosphoric acid he observed that, under certain conditions of current through the cell, the anode became not etched but polished. This phenomenon and the conditions governing it have become the object of a considerable amount of study by Jacquet and others and methods for the polishing even of large objects on an industrial scale have been developed for most metals and alloys. (Kemsley and Taggart, "Electrolytic Polishing" issued by the Commonwealth Scientific and Industrial Organization).

The actual mechanism of polishing is but imperfectly understood but it is noted that the polishing process is always accompanied by the formation of a viscous film which spreads more or less evenly over the anode surface. It is therefore presumed that the polishing action results from the preferential removal of metal from the tops of ridges where the film is thinnest. The composition of the film is not known accurately but must be some complex salt of the metal with the products of electrolysis. The thickness of the film depends on the current flowing in the cell and increases with the current until it becomes so thick as to be unstable. When this happens the cell current becomes unsteady and starts oscillating and it is under these conditions that

the best polishing results are obtained. The formation of the film is shown as a local maximum in a graph of cell resistance against current or potential difference as the film thickness increases to the instability limit. The current-P.D. characteristics of each cell for each electrolyte were determined giving sufficient time between each reading to allow the film to reach equilibrium thickness and a resistance-P.D. or a resistance-current graph drawn. The position of the maximum on this then acted as a guide to the best conditions at which to start making the final adjustments for the optimum current and P.D. settings. The accuracy of these settings can then best be determined from microscopic examination of the surfaces themselves. If the current is too low the surface film formed is not thick enough and the surface is etched by the electrolyte and if the current is too high the surface is generally polished but pitted as a result of gas evolution. The appearance at a magnification of perhaps 100 diameters of the surface under those two conditions is quite characteristic and can serve as a very reliable guide to the corrections required. The difficulty in achieving the best results is due to the very large number of variables involved. Once the best electrolyte has been chosen, the current, potential and cell geometry still remain as very important variable factors.

The enormous advantage of electrolytic polishing is, of course, that metal is being removed so that, in polishing, far from a cold-worked layer being formed, any distorted layer resulting from the preliminary preparation of the surface is removed and a pure lattice structure left at the surface. The preparation of the surfaces prior to polishing is not critical as polishing can, in principle, be continued until all the scratches have been removed. In general, the mirror blanks, stamped as discs out of sheet metal were merely ground down on progressively finer emery paper from grade F to 5/0. They were held in a brass guard ring holder so that there would be no tendency for the specimen to

be rounded at the edges. After polishing is completed the only treatment required is the washing off of the polishing film and in some cases, eg. tin, this is rather difficult and critical. If the film was successfully removed and the surface was regarded as satisfactory the specimen was washed in distilled water and ethyl alcohol, dried and kept in a dessicator over calcium chloride.

Polishing cells: The earliest cell used followed the orthodox pattern illustrated by Kemsley and Taggart. A perspex plate carried a cooling coil of german silver tubing through which water could be circulated and which also acted as the cathode of the cell. The specimen was supported horizontally at the end of a vertical anode support. A stirring paddle was driven by a small d.c. electric motor and the temperature was measured by a mercury thermometer. The electrolyte was merely contained in a glass beaker placed underneath the perspex plate. This arrangement proved very inconvenient to work with and gave very poor results with tin. Whether this was due to the electrical arrangement or the electrolyte is not known but, in any case, an entirely different type of bath was developed. This was based on the design of Elmore and is illustrated in figs. 10 & 11. The cell is constructed from the top part of a glass bottle from which the lower portion has been removed. It is inverted over the specimen which is held, face upwards in a brass cup into which the mouth of the bottle fits. This is connected to the positive lead of the power supply and leakage of the electrolyte between the mouth of the bottle and the specimen is prevented by a rubber ring seal pressed between them. A cylindrical cathode of metal, tin-plated steel or copper depending on the specimen, is slipped down inside the top of the cell and rests on the inside of the neck of the bottle. A wooden base on which the specimen holder rests is fitted with a clamp so that the cell could be pressed securely down on to the rubber seal.

This cell was made to fit the larger size specimens for the older cryostat. For the smaller specimens a similar cell was used. It was constructed

ELECTROLYTIC POLISHING APPARATUS

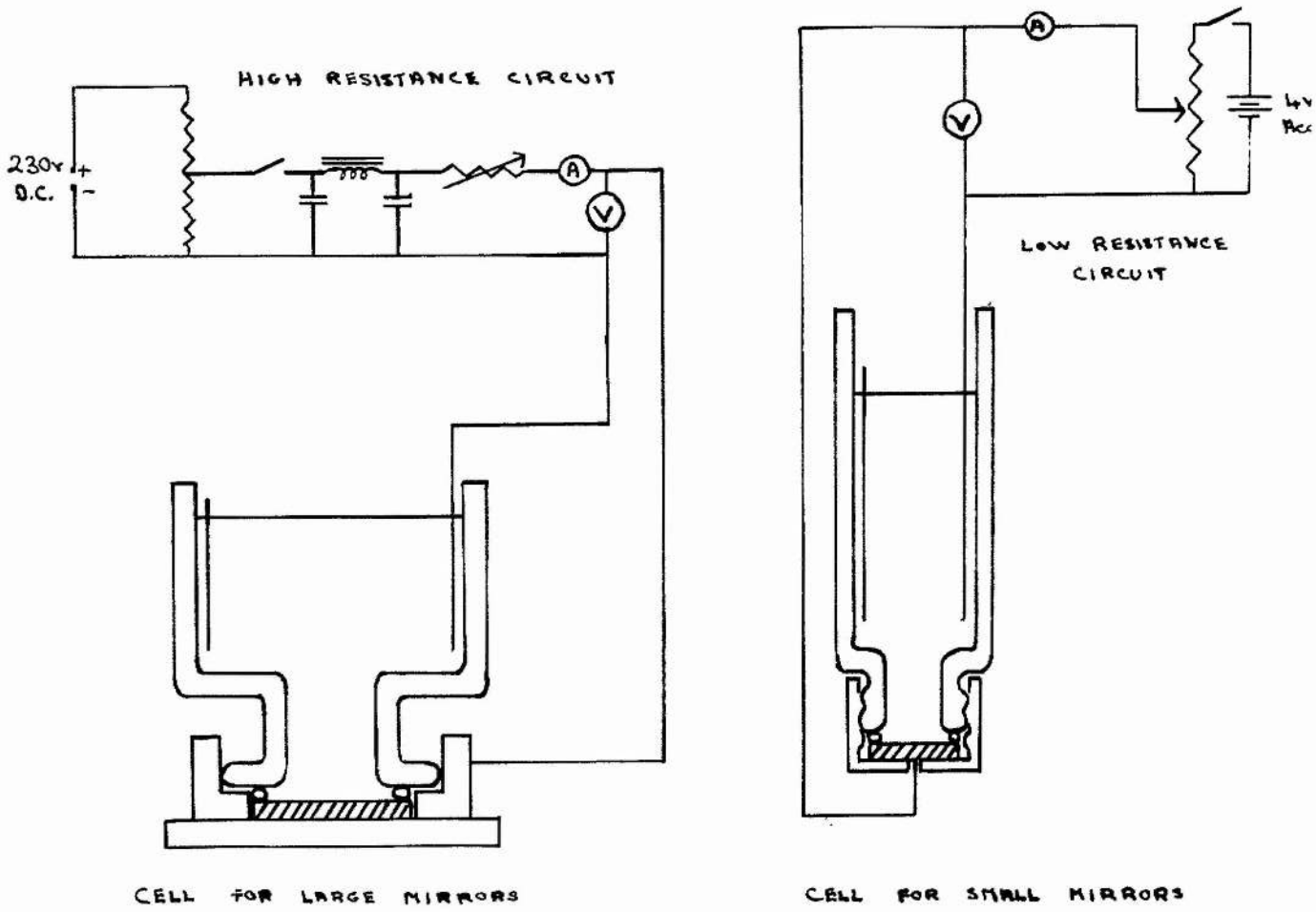
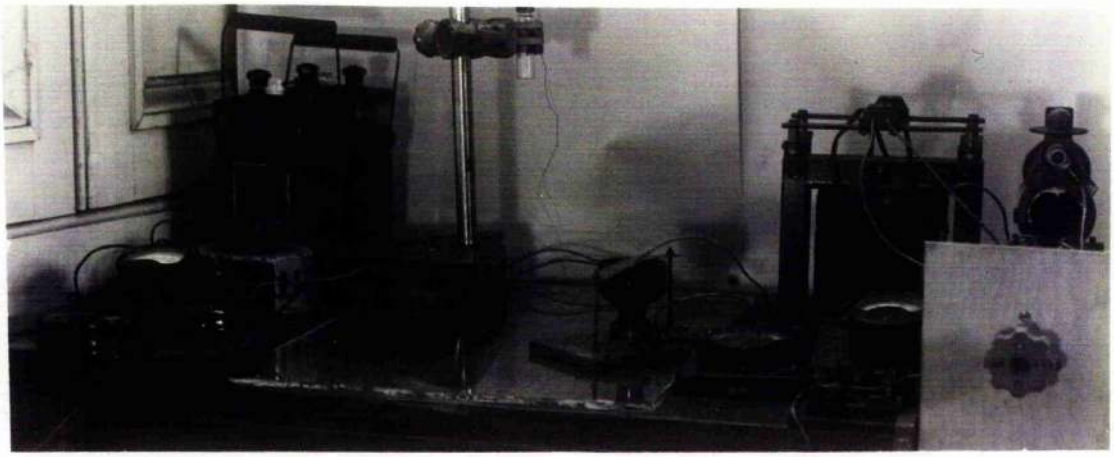


Fig. 10.



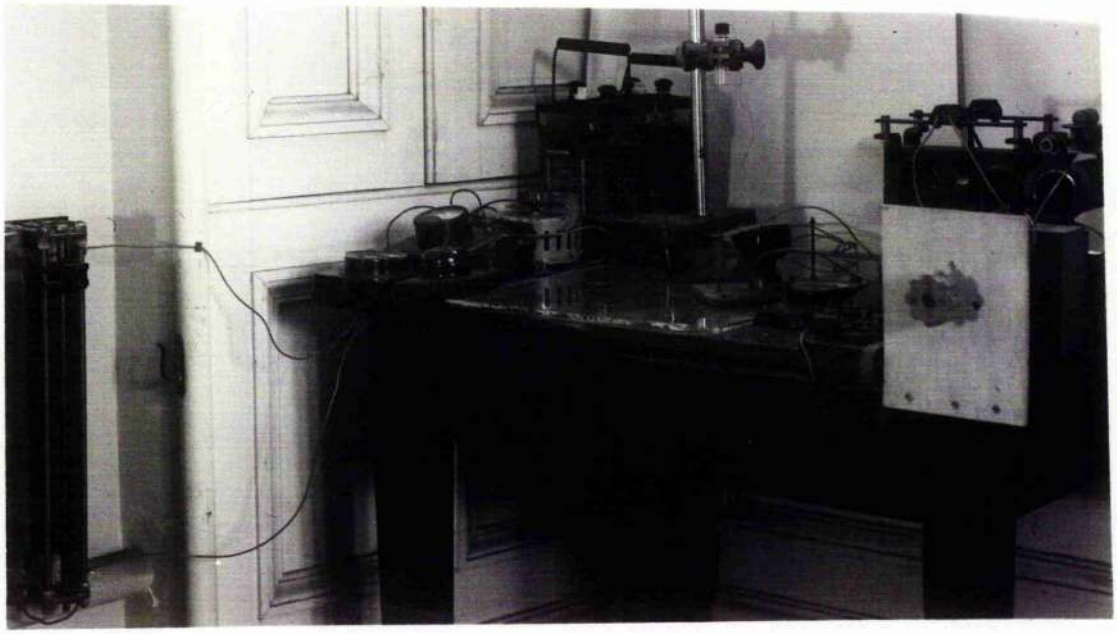


Fig. 11. General views of the electrolytic polishing apparatus with the high resistance circuits on the right and the low resistance circuits on the left

from a small glass vial with a plastic screw top. The specimen just fitted inside this and the thermocouple wires which were normally soldered to the back of the mirror were taken out through a hole in the cap to serve as the anode lead. A rubber ring seal was interposed between the specimen and the top of the vial which was screwed down to make a liquid-tight joint. The bottom of the vial was removed as in the cell for the larger specimens and when the assembly was supported vertically in a clamp the cell held about 10 cc. of electrolyte. A cylindrical cathode was used as in the earlier case.

The merit in this type of bath is its comparative simplicity and accessibility of the specimen for washing purposes. No provision is made for cooling but polishing times were kept so low that, with the current densities used, no appreciable heating resulted. It also automatically ensures that no foreign materials at the anode potential come into contact with the electrolyte and secures an uniform distribution of current density across the specimen surface resulting in more even polishing. The horizontal position of the specimen with its polished surface upwards also helps to maintain stability of the polishing film.

Power Supplies: There are two types of electrolyte in common use distinguished by the resistance of the cell and the types of power supply differ accordingly. In the case of high resistance electrolytes a fairly high potential of up to 100 v. is required to give an adequate current and the normal form of control is a variable resistor in series with the cell. An ammeter in series with the cell and a voltmeter across it enable the current-potential characteristics of the cell to be determined initially and the conditions during polishing to be controlled. In the present case the power is supplied by a 230 v. full wave rectifier, the potential from which was halved by a potential divider and smoothed by an L-C filter before passing to the bath through the resistor and meters described above. For low

resistance electrolytes, potentials as low as 4 v. suffice and are usually supplied to the polishing cell through a potentiometer. In the present case two 2 v. accumulators were used as a power supply and the cell was, as before, provided with the necessary voltmeter and ammeter. With this arrangement, the potential from the potentiometer is used to control the polishing conditions rather than the current as in the high resistance case.

Electrolytes and Conditions: The electrolytes used are those originally employed by Jacquet and listed by Kemsley and Tegart.

a) Tin: The solution used first with the earlier type of bath is as follows:

144 cc. ethyl alcohol
10 gm. aluminium chloride (anhydrous)
45 gm. zinc chloride (anhydrous)
32 cc. water
11 cc. n-butyl alcohol

This is a high resistance electrolyte and potentials of about 25 v. with currents of about 300 ma. were used. Various polishing times from 30 sec. upwards were used but the results were never satisfactory, the surfaces being invariably etched apparently by the film itself. Whether or not the lack of success was the result of unsuitability of the conditions or merely of inexperience as this was the first method tried is not known but, in any case, the method was abandoned.

With the second type of bath described above, another solution was used. It contained:

194 cc. perchloric acid (S.G. 1.61)
800 cc. acetic anhydride

This solution is extremely unpleasant to use. Apart from the explosive tendencies of perchloric acid, especially in the presence of dehydrating

agents, the acetic anhydride gives rise to dangerous and unpleasant fumes. The danger of explosion in the solution is greatly minimised by keeping it cool and precautions were invariably taken to keep the temperature below 30° C. The most dangerous time is when the solution is being made up as the heat of solution is considerable. The method adopted was to hold the acetic anhydride in a beaker surrounded by ice and water and to add the perchloric acid, diluted to the correct concentration, drop by drop from a burette at a rate of about one drop every five seconds. In this way the solution is kept adequately cool and the chance of the perchloric acid concentration rising to a dangerous value is eliminated. The solution was kept in a dark bottle in a cool cupboard and did not seem to deteriorate over a period of several months.

The polishing conditions for tin determined from a resistance-potential graph were about 17 v. with a total current between 1.5 a. and 2 a. The time of polishing varied with requirements but was usually about 2 to 4 minutes. Extreme care is necessary in the removal of the dark polishing film as it is essential to avoid the formation, in situ, of products of hydrolysis of the film material which etch the surface. The film must be washed off by a rapid stream of very hot water and a successfully polished surface results only if the whole film is washed off at the instant the water strikes the surface. With a little practice satisfactory surfaces were obtained and polishing times could then be extended for as long as was required by the initial state of the surface. It was found that a succession of short polishing times with intermediary washings gave more satisfactory results than one long polishing time and that it was much more difficult to polish the large area of the $\frac{3}{4}$" diameter mirrors than that of the $\frac{1}{2}$" diameter specimens.

b) Copper: Copper specimens were polished using an electrolyte consisting simply of orthophosphoric acid solution with a specific gravity

of 0.9. This is a low resistance electrolyte and the power supply was of the low potential type described above. The resistance-potential curve showed optimum conditions at about 0.9 v. and the currents used were of the order of 20 to 30 mm. Copper proved to be much easier to polish than tin. The polishing film seems to be more stable and presents no difficulties in washing. Individual polishing times were usually about 3 to 5 minutes and, after washing, polishing was continued for as long as necessary to obtain a satisfactory surface.

2) Casting Methods

Because of the time required to obtain satisfactory results for tin by electrolytic polishing, an alternative method for producing the mirror surface was sought and a technique of casting the surface against a flat glass plate was developed. The advantages of such a method are obvious in that, if successful and the conditions are correct, the surface formed is automatically strain-free and plane. The conditions for the formation of a satisfactory surface are firstly that the metal should wet the glass so as to secure as fine a surface finish as the glass and not leave any bubble pits or slag inclusions at the surface. This ensures that the surface is optically satisfactory and to satisfy the second condition that the surface be undistorted and strain-free, it is necessary to arrange that the metal at the surface is not exposed to strains or displacements arising from high temperature gradients. To satisfy these conditions the following method was developed.

A block of steel about 4" square and 3" thick to provide a large heat capacity was heated by Bunsen burners. A square glass plate about 1/16" thick which had been carefully cleaned and degreased with carbon tetrachloride with final washings in distilled water and alcohol before drying, was placed on top of the block and a small piece of tin resting on the plate showed

when the temperature of the glass surface reached the melting point of tin. The mould for the mirror was a brass cylinder of the appropriate outside diameter for the mirror holder and about $\frac{3}{4}$" to $\frac{1}{2}$" long. This rested on top of the glass during heating and, when the tin indicator showed that the temperature of the glass surface was above that of melting tin, the sample metal was melted in a silica boat. A hole drilled in the bottom of this at one end enabled clean tin to be poured out leaving the oxide layer behind. Enough tin was poured into the mould to cover the bottom and a thermocouple junction, wet with soldering spirit, was dipped into the tin surface and supported while the tin froze. This simultaneously ensured that the tin wet the sides of the mould, which is essential as the seal between the tin and the mould must be vacuum tight even when immersed in liquid hydrogen.

The whole assembly was then allowed to cool very slowly, turning down and removing one Bunsen burner at a time. The time required for the tin to freeze was about one or two hours and the time to cool down to room temperature about five or six. It is desirable to cool the tin as slowly as possible to avoid thermal strains and the question of oxidation at the reflecting surface during this time does not arise as we suppose that, by this time, the tin has wet the glass surface and is intimately in contact with it to the exclusion of atmospheric gases. When completely cool the glass was removed from the mirror, if necessary, by cracking it off in little pieces.

The most frequent defects were oxide inclusions and bubbles at the surface which reduced the amount of useful reflecting area. To eliminate these troubles, the temperature of the glass plate and molten tin had to be fairly accurately controlled. If the temperature of the plate was too high the tin oxidised as it covered the surface and if the glass was too cold, bubbles remained trapped on its surface. The actual temperatures were not measured but a little practice soon showed the correct conditions. The

temperature of the tin itself is not critical but was usually kept as low as possible to avoid undue oxidation during pouring.

If the conditions had been correct before pouring the tin wet the glass completely and the plate had to be cracked off. This left a plane, brilliant tin surface with only very slight imperfections due to a very few scattered bubbles of a fraction of a millimetre diameter. The conditions were not sufficiently closely controlled to produce large crystals and microscopic examination showed that the crystal size at the surface ranged from 1/100 mm. to 1/10 mm. Various fluxes and wetting agents were tried in an endeavour to improve the contact between the tin and the glass but without success. By far the best results were obtained with surfaces which were scrupulously clean.

3) Annealing Method

The case of silver required further consideration. The quantity available was much smaller than in the case of the other metals and so there was no opportunity to experiment as had been done with the others. The idea of electrolytic polishing was not attractive as, although silver is apparently easy to polish, large quantities of metal can be lost in unsuccessful polishing attempts and a lot of experimenting is required before the correct conditions are ascertained. The casting method is not precluded but is rendered much less convenient than for tin by the much higher melting point. Bearing in mind the requirements of a reasonably plane but definitely unstrained surface layer, it was considered that a satisfactory surface could be obtained by annealing methods. The principle is that, even in a distorted but polished layer which has been formed during grinding and polishing, heat treatment at a temperature above that required to produce recrystalization would lead to grain growth spreading through the distorted layer to reform an unstrained crystal structure right up to the surface. It is to be expected that this would result in a slight diminution of the degree of polish resulting from the alteration

to the crystal structure at the surface but, as has been pointed out previously, this should not be an important consideration when only the temperature variation of reflectivity is required.

The sample came in the form of wire which was melted down to a bead in a clean silica crucible. The bead was then hammered and rolled out into a disc which was, without being turned accurately circular, ground plane on one side on progressively finer emery papers. This face was then given a light polishing with alumina which left it with a reasonably brilliant surface but which did not, presumably, result in an undue amount of plastic deformation of the surface layer. The disc was then annealed in air at about 600° C for 1½ hrs. and then cooled slowly to room temperature. The disc was soldered with Wood's metal to a brass ring similar to that used as a mould for the casting of tin specimens to enable it to be mounted in the mirror holder like the other samples and a thermocouple was soldered to the back.

4) Nature of the Surface and Impurities

In the case of copper and tin, the samples were prepared from normal commercial sheet metal. The silver specimen was prepared from silver supplied by Johnson Matthey. The impurity content of the copper and tin is not stated but is unlikely to exceed .1% for copper and .02% for tin. That for silver is guaranteed to be less than .0001%.

Impurity addition resulting from processing must be very small in the case of those samples prepared by electrolytic polishing. Any surface impurity acquired during the preliminary treatment will be removed during the polishing process and no fresh contamination is likely to take place while the specimen is being polished. This will hold true for all the copper specimens all of which were electrolytically polished. It will also be the case for some of the tin specimens used earlier but the later specimens, to which the results quoted later refer, were cast. During the casting process contamination can

arise by the mixing in, on melting, of impurities present on the surface of the stock metal, by contact with the melting vessel, by oxidation in the air and absorption of gases while molten and, finally absorption of foreign material in the mould and on the glass surfaces. Contamination from dirty surfaces was minimised by the use of a clean silica boat in which the tin was melted and the high degree of cleanliness of the glass casting surface which was required to give a satisfactory mirror. As has been mentioned, visible slag contamination was avoided by straining the molten tin through a small hole in the silica boat so that the only appreciable source of impurity remaining is absorption of gases such as atmospheric oxygen. Since this goes into solid solution in tin no trace would be shown on microscopic examination and very little can be said about this type of contamination.

The original melting down of the silver specimen was done in air so that the possibility of oxide formation is present. In the initial, mechanical grinding particles of emery could be forced into the comparatively soft surface of the silver and would remain on the reflecting surface. The annealing took place in air and, while the temperature was kept as low as was consistent with a reasonable annealing time, oxide formation could take place although the extent of this was presumably negligible compared with the effect of the initial melting.

After processing the only metal likely to be further affected is copper which oxidises spontaneously at room temperature in air. However, we are concerned here only with bulk impurities rather than surface films which will be considered later.

The specimens were, in each case, examined microscopically in order to ascertain the surface structure and, for all three metals, the existence at the surface of a crystal lattice structure was verified. The grain size in the case of the tin specimen was 1/100 mm. to 1/10 mm. and was slightly

smaller for the copper and silver. The copper specimens were not annealed and so remained in the probably fairly highly worked condition resulting from the rolling. Examination of the silver surface showed no trace of the abrasive contamination which has been suggested above.

Chapter 6

The apparatus had been designed for the detection of small changes in reflecting power occurring over small temperature ranges as the work contemplated had been concerned largely with changes in reflectivity over the superconducting transition. The problems of temperature control and measurement under these circumstances are relatively simple as the temperature range involved would be that attainable using liquid helium. However, it appeared that work of this nature would not be possible and that the most profitable temperature range to study would be that between room temperature and that of liquid hydrogen. To achieve this with the apparatus available the only technique is to cool the cryostat and then take measurements as the cryostat heats after all the liquid has boiled away. This then necessitates the use of thermocouples or some other means of temperature measurement and, apart from recooling the cryostat with more liquid air of hydrogen, the only temperature control possible is to accelerate the heating using the heating coil. This heater requires relatively heavy leads which would be bad if the heat leak to the mirror holder were an important consideration but which were permissible under the present circumstances. Further difficulty arises from the fact that all the critical parts of the apparatus are enclosed in the vacuum space during the experiment so that very little could be done in the event of anything going wrong and any breakdown usually meant waiting for the cryostat to heat up and admitting air to the tank before any adjustments could be made and the tank re-evacuated to start again. The situation was made rather easier by the use of a thick glass plate on the unused cryostat mounting over the reference mirror which enabled the working of the apparatus, but not the state of the mirror, to be observed.

1) General Experimental Procedure

In setting up the apparatus for normal operation the optical system was adjusted outside the tank as far as was possible without the specimen mirror. It was then pushed into the tank and the cryostat inserted. The cryostat was rotated and tilted until, with a piece of ground glass substituted for the detector, it could be seen that the two beams from the sample and the reference mirror were suitably placed to fall on the detector. A certain amount of further adjustment was possible by sliding the whole optical system on the rails so as to move it with reference to the sample mirror. This was not a very critical adjustment and, once a suitable position had been found, a bolt screwed into the inner end of the optical bench acted as a stop to make the setting reproducible. The shutter in the reference beam was then set so that, with the specimen beam shutter about 1/3 to 1/2 open, the beams were of about the same intensity. The detector was inserted and the end plate mounted so that the chopping wheel could be driven. The apparatus was started and a search made for a balance point made by moving the specimen beam shutter. When a minimum of the output signal had been found, the apparatus was opened to check that the specimen beam shutter was in a suitable position at the balance point to allow for considerable increase or decrease of the specimen's reflectivity. Any correction necessary to bring the balance setting of the specimen beam shutter to a suitable position could be carried out by moving the reference beam shutter. When a satisfactory setting had been found the specimen beam shutter was set to be just closed and the revolution counter and the pointer on the control handle set to read zero, if necessary by slipping the bevel gears driving the shutter. The apparatus was then ready for evacuation.

When the pressure was low enough the liquid air trap on the Pirani gauge and the shield round the specimen were filled in an endeavour to remove

pump oil and other vapours from the system before the mirror was cooled. The cryostat was filled either, in the case of liquid air, by pouring in through the filling tube or else, for liquid hydrogen, by using a transfer vessel. This was a glass dewar vessel fitted with a brass cap which, after filling at the liquefier, could be supported on a retort stand beside the apparatus. (See fig. 3). A vacuum-jacketed transfer tube could be fitted into the filling tube on the cryostat and screwed down to make a gastight seal. The vapour outlet from the transfer vessel was connected by rubber tubing to the atmospheric pressure return line and the hydrogen was transferred by opening the valve on the transfer tube and closing the gas tube from the transfer vessel. During filling the cryostat was open through the blow-off tube to the atmospheric pressure line and, when sufficient hydrogen had been transferred, as judged from the amount remaining in the glass dewar, the transfer tube was closed and the cryostat outlet switched to the pump. In the case of both liquid hydrogen and air, the technique was to transfer just enough liquid to leave a few cc. in the cryostat and then to pump to obtain the lowest possible temperature. Readings were started at that point and continued as the cryostat warmed up when all the liquid had evaporated.

2) Temperature Variations of Reflectivity

The readings were started by opening the specimen beam shutter until a minimum deflection on the output meter was obtained. This first reading means nothing by itself but it sets the specimen beam at a standard intensity. This can be maintained during the experiment by moving the shutter so that, thereafter, the changes in shutter setting from this first one are (after correction from the shutter calibration graph) inversely proportional to the change in reflectivity from the initial value. The apparatus was kept permanently balanced during the experiment so that measurements were made merely by reading the pointer and readings were taken every three or four

degrees as the temperature rose. The apparatus warmed quite slowly giving ample time for measurements and, as the warming rate decreased at higher temperatures, a controlled amount of heating was provided using the heater on the mirror holder. Readings were normally continued until one was made at $0^{0}C$ but, in the case of copper and tin, the measurements were extended upwards from $0^{0}C$ by heating the cryostat using a steam jet. During these higher temperature experiments the apparatus was still evacuated to avoid the possibility of contamination of the hot surface of the mirror in air.

Normally only one filter was used during each experiment but, when liquid hydrogen was used, heating was continued only so far as to overlap with readings obtained using liquid air. The filter changer was then used to place another filter in the beam, the cryostat was recooled and the experiment repeated.

The results are thus obtained as a set of angles, expressed in degrees, through which the specimen shutter control shaft has turned. If a large range of reflectivity has been covered the readings require to be converted, using the shutter calibration graph, to a set of numbers representing the actual area of the aperture uncovered but if only a small reflectivity range has been found, as was normally the case, the error introduced by taking the angles themselves as being proportional to the changes in aperture area is negligable compared with that arising from other sources. We now assume that the transmitted intensity is proportional to the area of aperture exposed and since only the central, uniformly illuminated portion of the beam is accepted, by the aperture, this is probably justified. We can thus say that the reflecting power of the specimen is inversely proportional to the exposed area and so the ratio between the reflectivity at any temperature R_t and that at the standard temperature, taken arbitrarily to be 273^{0} K. R. is:

$$\frac{R_t}{R_o} = \frac{A_o}{A_t}$$

where A_t and A_o are the corresponding aperture areas or angles. For each wave-length, this process leads to a curve of reflectivity against temperature of which each value is expressed as the ratio of the reflectivity at that temperature to the reflectivity at 273° K.

3) Wave-Length Variation of Reflectivity

To take account of the wave-length variation of reflectivity it is necessary to compare the reflectivities for different wave-lengths at one temperature only. This temperature is, in principle, unimportant but, for convenience, was taken to be 273° K and the procedure for obtaining the wave-length variation was simply to change the filters using the mechanical changer and obtain a balance point for each wave-length while the temperature remained constant. Since we are still restricted to ratios, the reflectivity for each wave-length was expressed in terms of that for the blue filter. Although the filter holder held only four filters, the reflectivity for any number of wave-lengths can be measured (as with temperature ranges) by using one in common between two sets of readings so that the ratios may be continued from one set to the other. This procedure does not take account of the wave-length variation of the reflecting power of the reference mirror and this must be measured in a separate experiment to be used as a correction. It was done by comparing the intensity of the light reflected from the mirror with that of light of the same spectral distribution as the incident beam. The place of the sample mirror was taken by an electric light bulb similar to the normal source and run in series with it. The filters were placed immediately in front of the detector so that the balance point would depend only on the amount of light reflected from the reference mirror for each wave-length. By obtaining balance points for each filter the reflectivity for each wave-length could

be expressed as a ratio with that for the blue filter. The readings gave directly the square of the variation as both the beam-splitting mirror and the reference mirror (which are of identical material) are involved. To simplify the conditions the main collimating mirrors were removed and the beam which normally falls on the specimen was displaced. The collimating mirrors are common to both beams when the apparatus is in normal operation so that their reflectivity does not enter into any correction. The curve obtained for the wave-length variation of reflectivity of the reference mirror was then applied as a correction to all the readings obtained for the sample. Having obtained the corrected wave-length variation for the sample as a proportion of the reflectivity for the blue filter at 273°K it was then possible to express every reading for that sample as a fraction of the reflectivity for the blue filter at 273°K. The readings are thus reduced to a common scale and give a complete picture of both temperature and wave-length variations.

The curves obtained in this way for copper, tin and silver are shown in figs. 12, 13, 14, respectively (See Tables XI to XIX). The curves were obtained using two tin mirrors, one cast and one electrolytically polished, two copper mirrors, both electrolytically polished and one silver mirror. The wave-lengths indicated are the values appropriate to the peak of the transmission curve or, if necessary, the peak of the combined sensitivity of the filter and detector. Each curve is made up of a number of anything up to five runs. The wave-length variations for copper, tin and silver at 273°K and for aluminium at 288°K are shown in fig. 15. The wave-length variation for any other temperature can be obtained simply from any vertical section across the temperature variation curves.

4) Absolute Reflectivity

Absolute measurements of reflecting power or even comparison of the reflectivity of different metals was never attempted but, if necessary, a

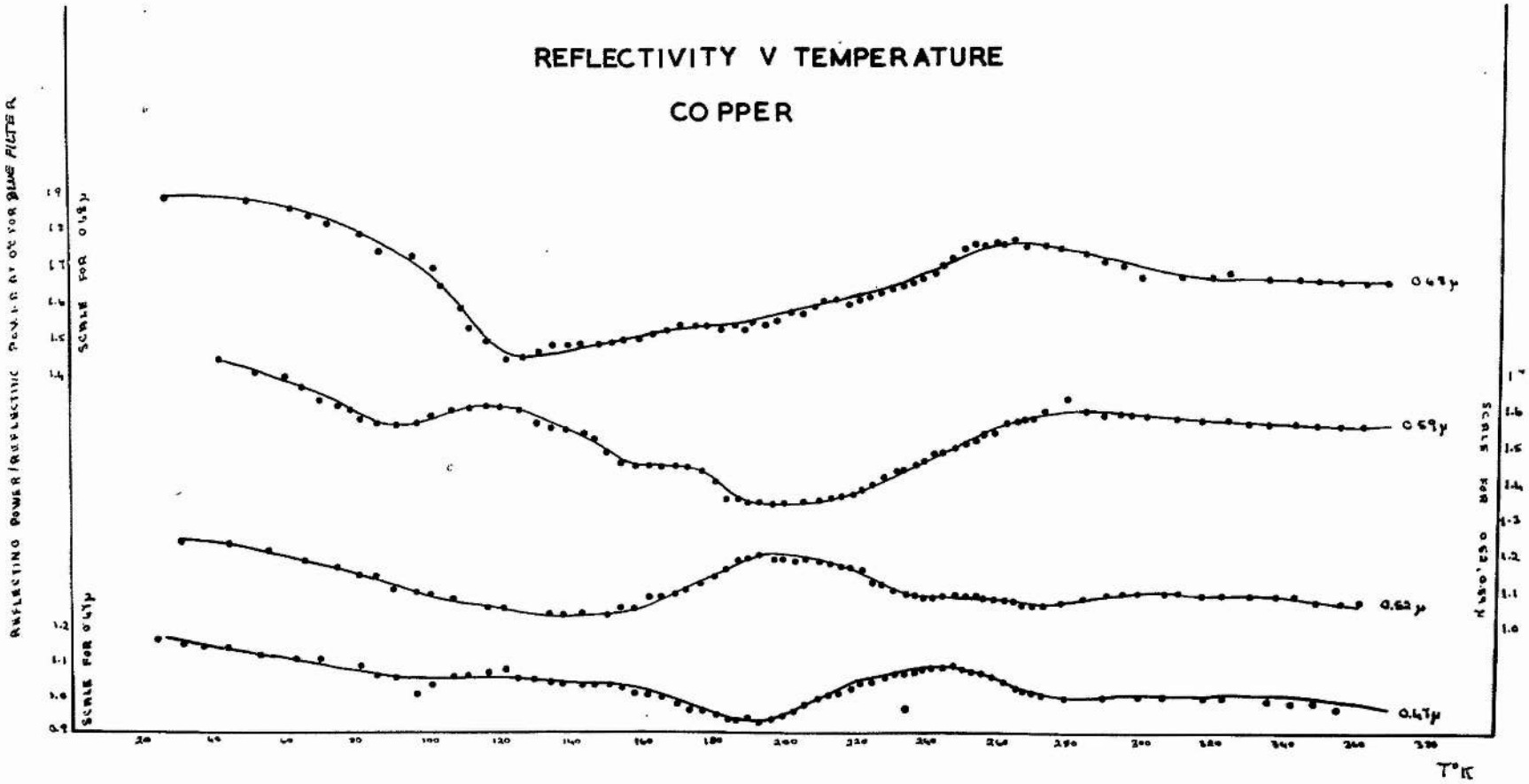


Fig. 12.

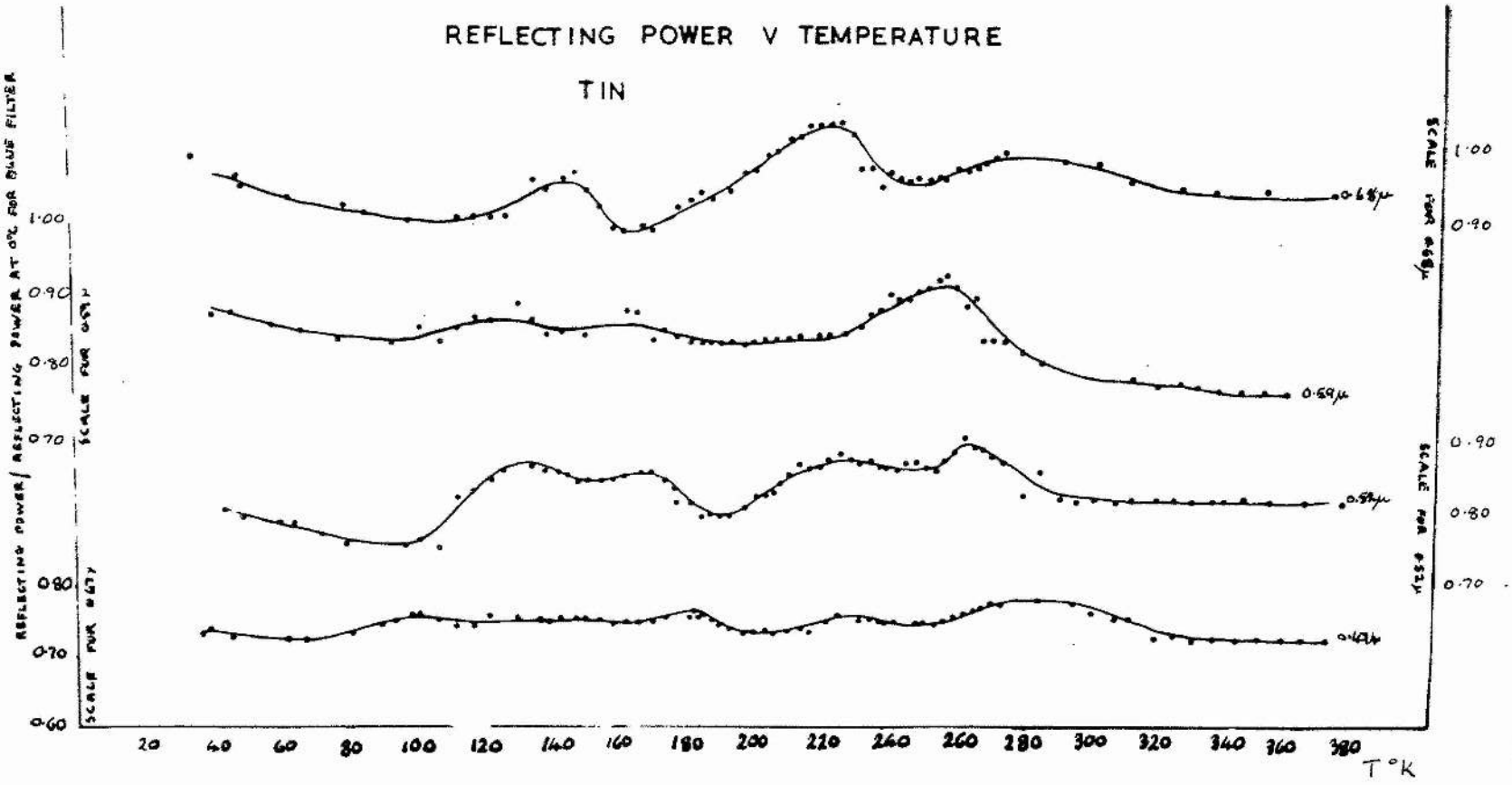

REFLECTING POWER V TEMPERATURE
TIN
REFLECTING POWER / REFLECTING POWER AT 0°C FOR BLUE FILTER
SCALE FOR 0.47μ
SCALE FOR 0.57μ
SCALE FOR 0.68μ
SCALE FOR 0.52μ
1·00
0·90
0·80
0·70
0·60
0.68μ
0.59μ
0.52μ
0.47μ
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
T°K

Fig. 13.

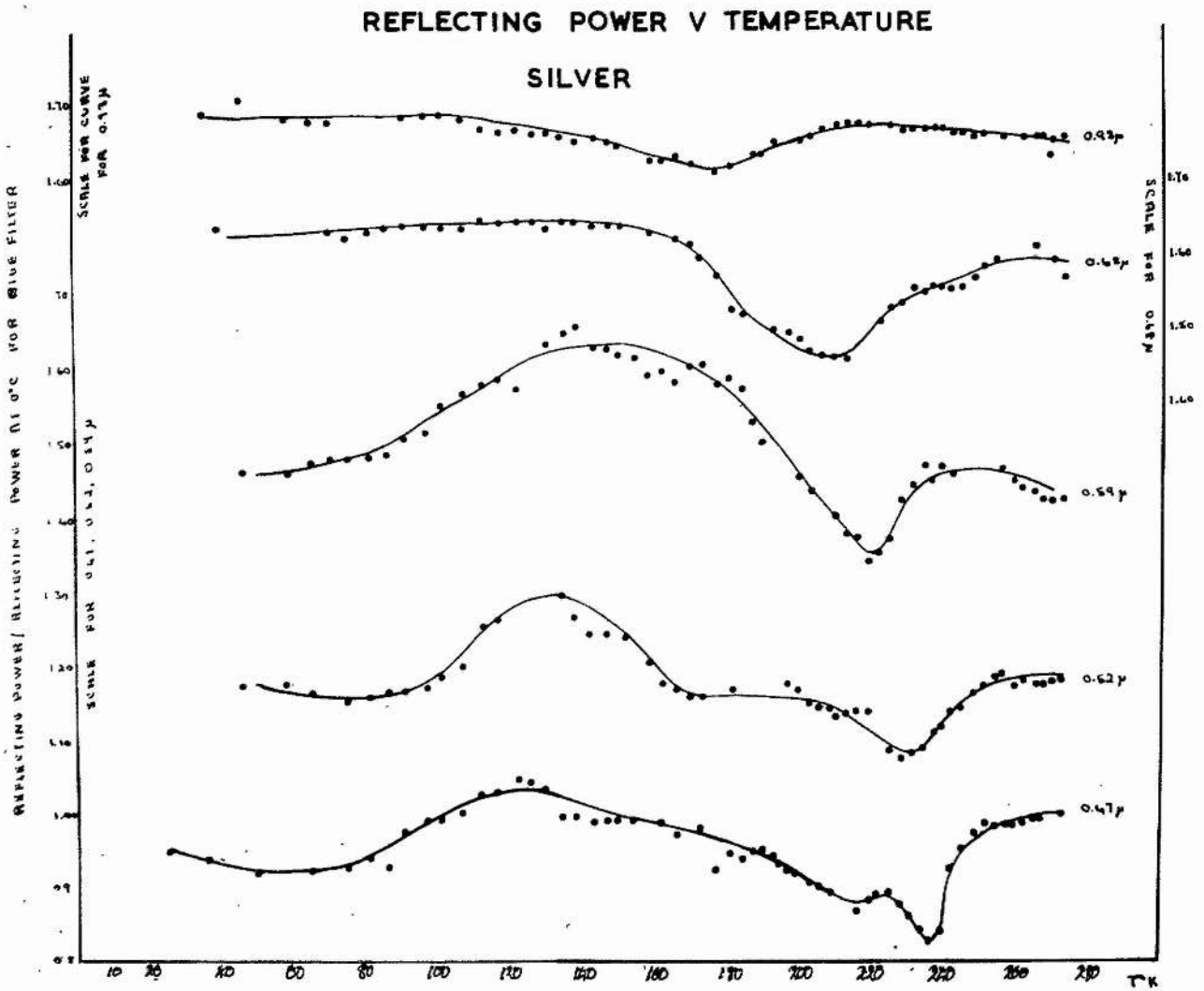

REFLECTING POWER V TEMPERATURE
SILVER
REFLECTING POWER AT 0°C FOR BLUE FILTER
SCALE FOR CURVE FOR 0.47μ
SCALE FOR 0.41, 0.44, 0.54μ
SCALE FOR 0.59μ
0.47μ
0.52μ
0.59μ
0.68μ
0.93μ
T°K

Fig. 14.

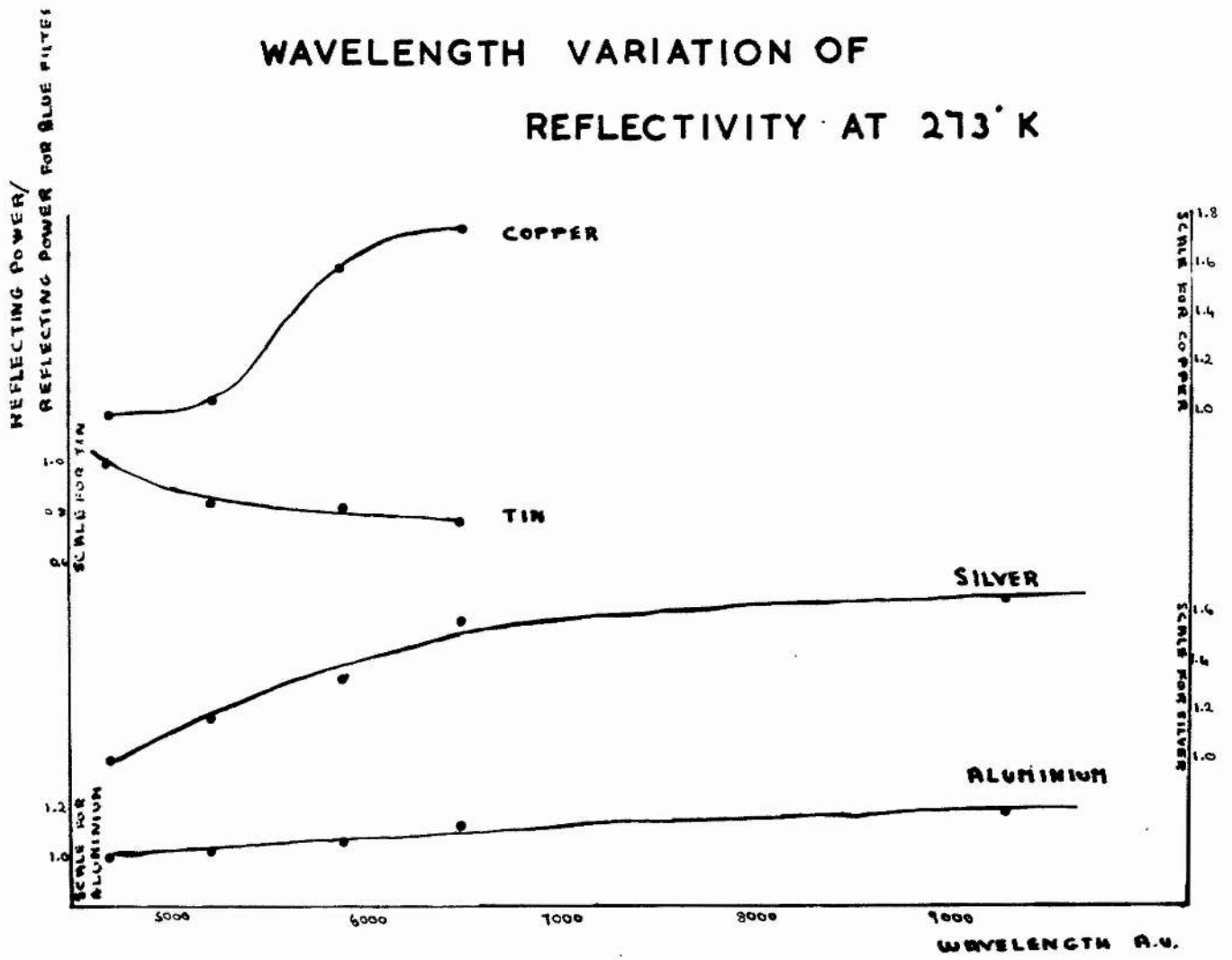

WAVELENGTH VARIATION OF
REFLECTIVITY AT 273° K
REFLECTING POWER/
REFLECTING POWER FOR BLUE FILTER
COPPER
TIN
SILVER
ALUMINIUM
SCALE FOR TIN
SCALE FOR ALUMINIUM
SCALE FOR COPPER
SCALE FOR SILVER
1.0
1.2
1.4
1.6
1.8
5000
6000
7000
8000
9000
WAVELENGTH A.U.

Fig. 15.

direct comparison between two metals could be made with the apparatus. Absolute values could then be obtained if comparison with a metal of known reflectivity were possible. The considerations involved in such an experiment are as follows. Firstly the incident beam ought to be smaller than the specimen so that all of it is reflected and no complication is caused by specimens of differing size. The second important condition is that all the light reflected from the specimen must reach the detector. These two considerations together require that the beam must be limited before it reaches the specimen to such an extent that it is smaller than both the specimen and the aperture just before the controlling shutters. This last condition now means that this beam cannot be used for measuring purposes as its position in the aperture is arbitrary and the setting of the shutter is meaningless. This shutter will therefore have to be left fully open and all measurements obtained by controlling the intensity of the other beam. The only conditions to be satisfied by the reference beam are that it is uniformly illuminated across its area and is of such an intensity that it balances with the beam from the sample at a reasonable reading on the scale. Having obtained a balance point with the sample, it would be replaced by the standard and the new balance point would lead to a value for the ratio between the reflectivities of the specimen and the standard. In experiments of this nature, it would be desirable to mount the specimens on the optical bench rather than the cryostat so as to secure reproducible geometry and to ensure that the beams from the specimen and the standard with which it is compared in the second experiment fall on the same part of the detector receiver. Provided the above conditions are satisfied no systematic error can arise and the accuracy of the determination would be limited only by random errors in the actual measuring.

5) Sources of Error

a) Measuring Apparatus

Random error in the normal reflectivity measurements arises from the reading of the meter which indicates the zero of the signal and of the scale which gives the total angle turned by the shutter control rod. The accuracy of the meter reading is limited by random movement resulting from spurious signals which can arise at a number of points throughout the apparatus. However the stability of the apparatus was generally such that the light spot on the output galvanometer could be observed using a magnifying lens and no random, short period movement was detectable. Any slower but possibly larger scale changes such as drift of the galvanometer zero do not matter as the signal is always adjusted to a minimum whatever its value when the balance point is being found. The sensitivity of the apparatus depends on the amount of light available but, during normal working, a change of 1° on the control handle pointer produced a detectable deflection on the output meter. The total angle turned to that point could have been perhaps five revolutions of the shaft so that the sensitivity becomes 1/(5,360) or .05%. Although these settings are the only quantities used in measuring the reflecting power and they should be, ideally, accurate to that extent, it would be unreasonable to claim this accuracy for the results. The factors limiting the accuracy are mostly of a random nature of the form of disturbances making it difficult to find the balance point. Noise in any of the electrical circuits or microphonics in the amplifier blur the balance point and stability of the source of light is important. Slow changes which occur over periods of more than a few seconds do not matter but any short period flicker, whether periodic or random, is undesirable. Exactly at the balance point it would have no effect as it would affect both beams equally but, while the balance point is being found, a random disturbance

Makes it almost impossible to determine the balance point. The magnitude of these effects is very difficult to estimate and varies from time to time but, in general, it seemed that settings could be made which were consistent to within $\frac{1}{2}$ to $\frac{1}{2}\%$.

b) Cryostat

Systematic error in the measurements can arise from any effect which can alter the specimen beam intensity. These effects can be associated either with the apparatus or with the surface of the specimen itself and it will be necessary to distinguish between these effects and those arising from genuine changes in reflectivity of the specimen.

The only mechanical effect due to the apparatus is warping of the cryostat. Any change in angle made by the sample mirror with the incident beam which is not uniformly illuminated falls on the aperture, considerable errors will be introduced. This results from the fact that, if this happens during an experiment, the resultant change in transmitted intensity will be interpreted as a change in reflectivity and also that the shutter calibration is no longer accurate if the aperture is not uniformly illuminated. Although the reflected beam admittedly turns through twice the angle turned by a rotating mirror, a beam movement of at least 5° is required to produce any significant error and warping of the cryostat to the extent needed for this is unlikely even considering the large temperature gradients in the cryostat. As explained earlier, all critical parts of the optical system after the beam splitting mirror are mounted on a rigid brass plate so that errors due to warping of the system itself are almost impossible. It is, further, most unlikely that any change should take place during an experiment in the reference mirror or the transmission in general of the reference beam. The variation in sensitivity over the detector cathode would result in spurious changes if the detector were moved during an experiment but the rigid clamping used must prevent this.

c) Mirror Surface

The only other factors influencing the reflected beam in addition to genuine reflectivity changes are alterations in the state of the surface of the specimen. No matter how carefully a surface is prepared, the formation on it of a film even of transparent material will alter the value of the reflectivity. The presence of at least an absorbed air film is unavoidable, as is well known from experiments on the photoelectric effect, unless the surface is not only maintained but actually prepared in a vacuum. Furthermore, although the mirrors were kept in a dessicator and never touched, the process of soldering them to the cryostat, although done at as low a temperature as possible, at least meant contact with the vapour of the flux and possible oxidation. Although exposure to air was unavoidable during this and subsequent adjustments of the apparatus, the tank, once evacuated at the beginning of a series of experiments, was usually maintained continuously at low pressure for several weeks. However, although evacuation is superficially desirable, it is not the complete answer. An oil diffusion pump was used which was fitted with neither a baffle or liquid air trap between it and the tank and this resulted in a certain amount of deposition of pump oil over the inside of the vacuum system. The situation is worsened by the fact that, during a large part of the time that the pump was working, the mirror was cooled giving the most favourable conditions for deposition on it. This was minimised by attempting to clean the vacuum by filling the liquid air shield around the mirror and the trap at the Pirani gauge before the mirror was cooled but, over a period of weeks, the growth of a film of pump oil and other materials degassing from the tank walls is probable.

The case of a reflecting surface covered with a transparent film has been treated by Drude. He showed that, even when the film is completely transparent the reflectivity of the surface is diminished by an amount depending on the refractive index of the film material and that the optical constants

derived from the reflection of polarised light are even more seriously affected. Were this a constant effect it would not be of any significance in the present experiments where only changes are considered but the film material is bount to show some kind of dispersion which will thus affect the wave-length variation of reflectivity of the sample. However, the biggest effect will probably be on the temperature variation. The variation with temperature of Drude's effect is likely to be small but the main trouble will arise from changes in state of the film. Over such a large temperature range some condensation phenomena can be expected and since the film will probably be of mixed composition, the resultant change in transparency of the film is likely to be complex and spread over a fairly large temperature range.

The case of copper is additionally complicated by the presence on the surface of the oxide coating which forms on mere exposure to air at room temperature. Even without the heating required for soldering this is visible as a dulling and reddening of the surface and with moderate heating up to 100°C or so, will grow quickly to a thickness which will show interference colours. Friction experiments (Whitehead 1950) demonstrate the existence of the film on specimens freshly polished electrolytically before it has become thick enough to be visible to the naked eye and its thickness under those circumstances has been estimated as up to 100^{0}A. The effect of temperature on this film is difficult to estimate but is presumably small. The main disturbance is of the wave-length variation where it has the effect of reducing the reflectivity at the blue end of the spectrum. Disturbance due to the above effects is undoubted worst over a large temperature range as it is very difficult to ensure constancy of conditions over the whole range from 20°K to room temperature. Although possibly still present, they would be much less important if changes over only a small temperature range were to be considered.

Other stray effects such as scratches, imperfections and lack of

planeness are not important if only changes are being measured and result only in loss of light. The impurity content is likely to be small and, as we are working at temperatures where the residual resistance of the sample is negligible compared with the thermal resistance, the impurity is not likely to have much effect on small scale conduction processes like the optical properties. The results obtained by Lowery, Bor and Wilkinson (1935) on the reflectivity of a series of alloys of copper and nickel show that the absolute reflectivity is altered to only a slight extent by the addition of the solute metal and the form of wave-length variation is virtually unchanged. We can therefore expect that the effect of any stray impurity which must have a much lower concentration than was used by Lowery, Bor and Wilkinson must be very small.

Unfortunately it was impossible to undertake experiments to check all the above points and appropriate caution must consequently be used in interpreting the experimental results. The optical properties of surfaces are notoriously difficult to explain in detail and irregular experimental curves with discrepancy in small scale changes between different observers is relatively common. The present results involve only changes which may be a little more reliable but it is probably unjustifiable to draw conclusions from more than the general outline of the curves.

6) Resistivity

Since the d.c. conductivity of a metal is so closely connected with the reflecting power, the conductivity was measured of samples of metal treated, as far as possible, in the same way as the mirrors so as to reproduce the conditions existing in the mirror material. The specimen, in the form of a rod or wire, had potential and current leads soldered to it and the resistance was measured using a calibrated ammeter and the Doran potentiometer. Currents of the order of 1/10 amp to 1 amp were used and were obtained from storage batteries. A thermocouple for temperature measurement was soldered to the

centre of the specimen and the emf. from it applied to the second channel of the potentiometer. The specimen was either kept as small as possible or else coiled up so as to minimise the chance of thermal gradients in it. The measuring technique used was, again, to cool the specimen and make the measurements as the apparatus heated to room temperature. The specimens were cooled in a glass dewar which had its mouth closed by cotton wool and measurements were made down only to liquid nitrogen temperatures. It was found that, if sufficient liquid nitrogen were used that the whole dewar was cold before heating started, the temperature was uniform to within the sensitivity of measurement over a volume amply big enough to contain the specimen and that the heating rate was very stable.

The length of the specimen between the potential contacts, which was usually about 10 cm., was measured using vernier calipers and the diameter, which ranged from about ½mm. in the case of copper to 3mm. for tin, with a micrometer screw gauge. The silver specimen was prepared from wire which was annealed under the same circumstances as the mirror. The tin specimen was cast into a pyrex capillary under the same conditions of temperature and cooling rate as the mirrors and were prepared from the same material. The copper sample was formed from commercial high conductivity wire. This was not annealed so as, again, to give roughly the same conditions of grain size and internal working as the mirror sample. The correspondence between the two samples in the case of copper is not too exact but it will be seen that only the silver results are used in computing to compare with the reflectivity results.

The curves for resistivity against temperature are shown in figs. 16, 17, 18, (see tables III, IV, V). It can be seen that the curve for silver is apparently linear and shows no interesting features. The copper curve is linear from room temperature down to about 135°K where an increase in slope occurs until it flattens off again at about 105°K to a slope less than that

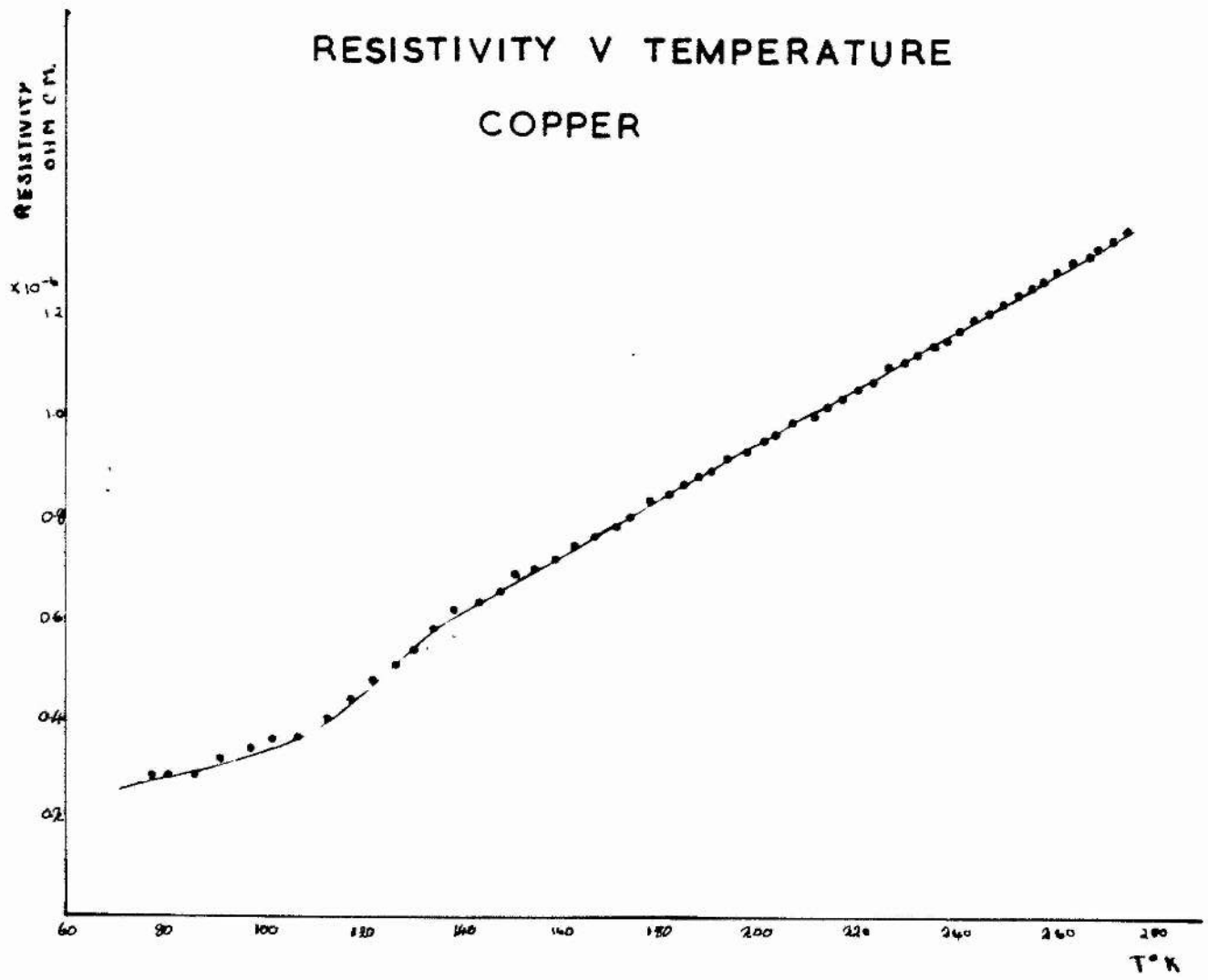

RESISTIVITY V TEMPERATURE
COPPER
RESISTIVITY OHM CM.
X 10⁻⁶
1.2
1.0
0.8
0.6
0.4
0.2
60
80
100
120
140
160
180
200
220
240
260
280
T° K

Fig. 16.

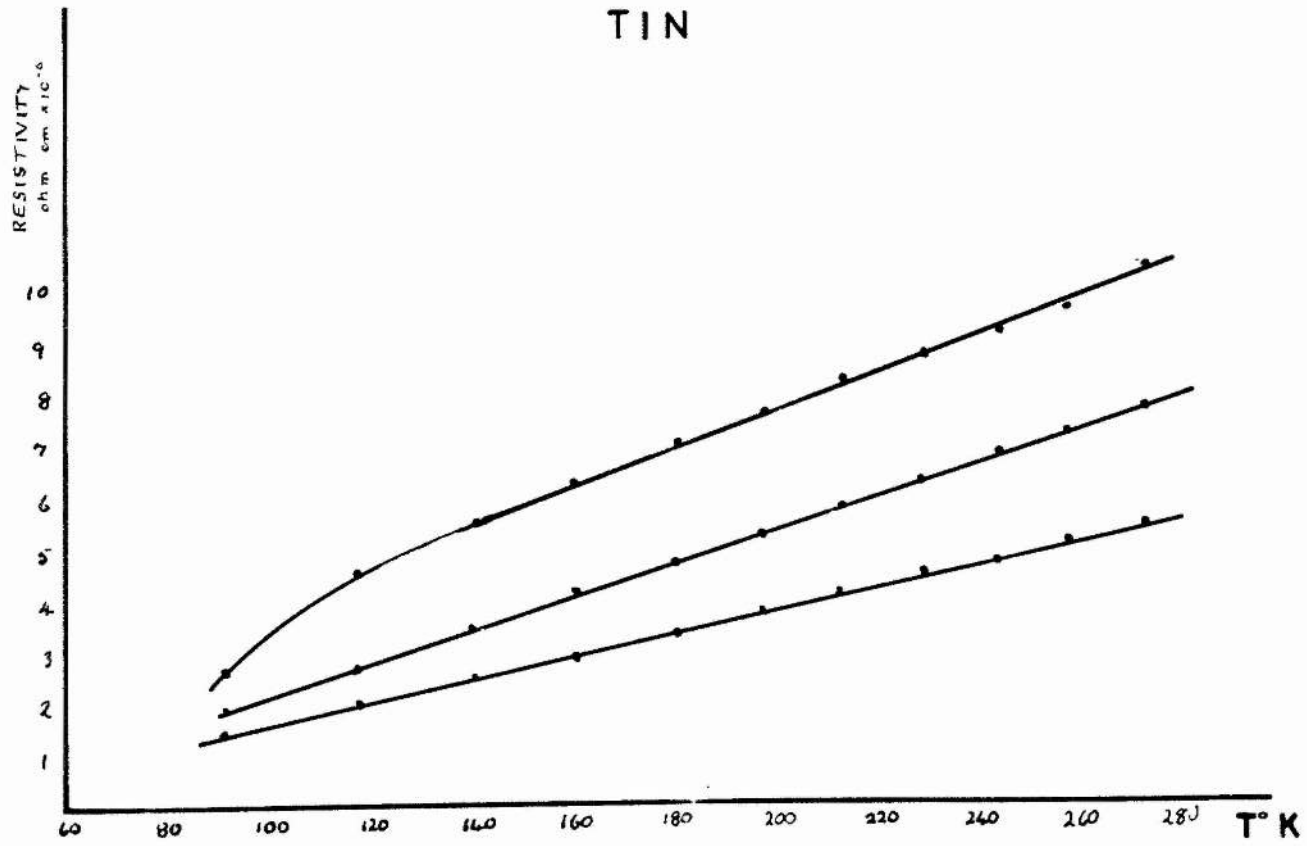

RESISTIVITY V. TEMPERATURE
TIN
RESISTIVITY
ohm cm x 10⁻⁶
10
9
8
7
6
5
4
3
2
1
60
80
100
120
140
160
180
200
220
240
260
280
T° K

Fig. 17.

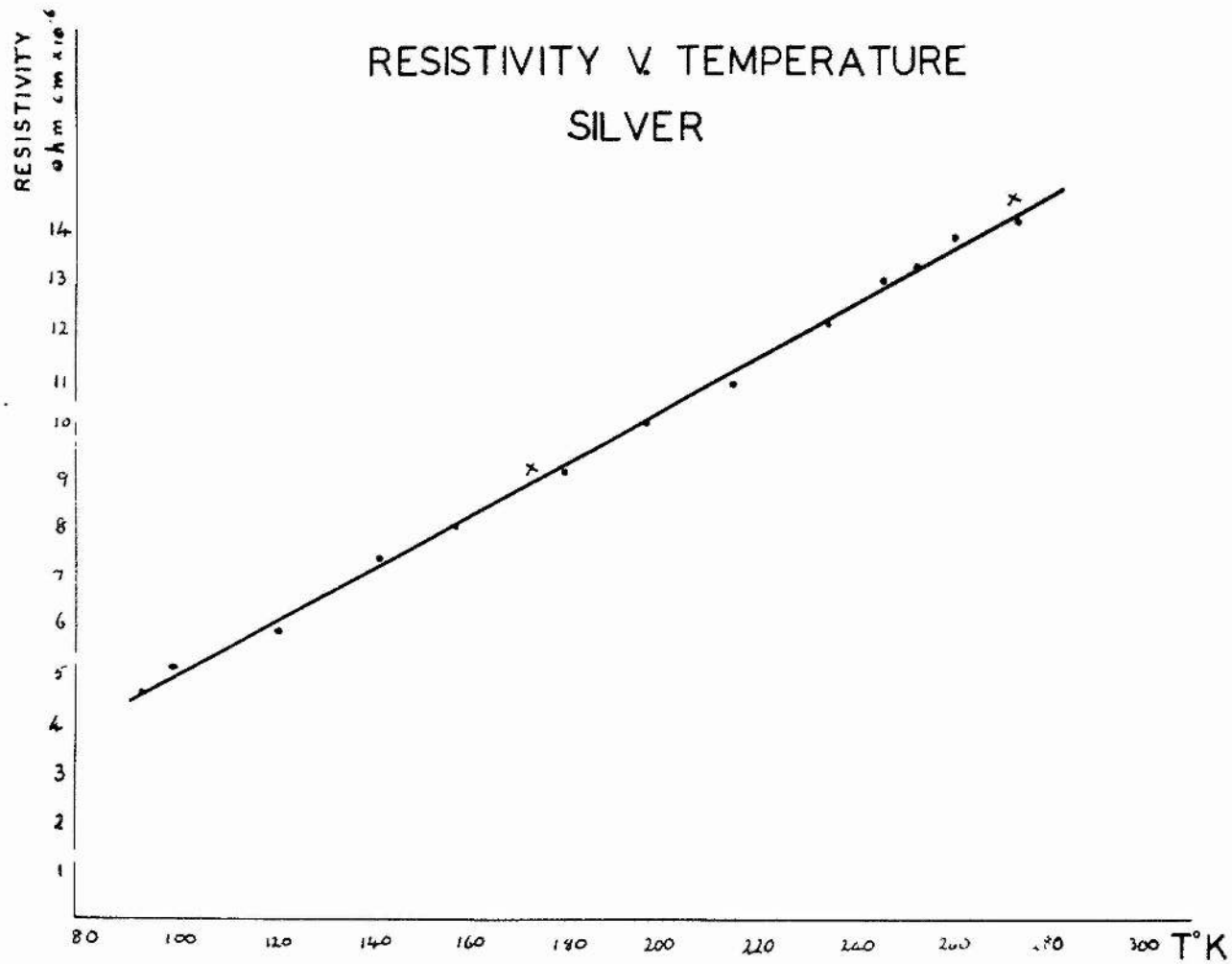

RESISTIVITY V. TEMPERATURE
SILVER
RESISTIVITY ohm cm x 10⁻⁶
14
13
12
11
10
9
8
7
6
5
4
3
2
1
80
100
120
140
160
180
200
220
240
260
280
300
T°K

Fig. 18.

above 135°K. This curve is made up of a number of runs confirming the reproducibility of the effect. Of the curves for tin, the centre one corresponds to the freshly cast specimen, the lowest to the same specimen measured about three days later and the uppermost to the same specimen drawn through dies to give a cross sectional area reduction of about 70%. Temperature control in these last experiments on tin was sufficiently good that readings could be made repeatedly at the same temperature on both cooling and warming so that only mean values are plotted for each temperature. The average scatter between readings at the same temperature is about 1%. Thus the change in slope which appears at about 120°K cannot be the result merely of scatter as the deviation from the straight line at 91°K is about 30%. The crosses mark the points listed by the Handbook of Chemistry and Physics and refer to "pure annealed" copper, "99.98% electrolytic" silver and the tin is unspecified.

The maximum reading or systematic error in either of the electrical quantities used in determining the resistivity was about ½% and the predominant error in the mechanical measurements is that of the radius of the sample. In the worst case, that of copper, this could amount to about 1% and so the total maximum expected error is a little over 1%.

7) Columbium Nitride

A sample of columbium nitride presented by Dr. D.H.Andrews was available and it was desired to investigate the behaviour of the cryostat under controlled pumping and, at the same time, to observe the superconducting transition which occurs in columbium nitride at about 15°K. The columbium nitride was available only in small flakes and one flake was mounted on a plastic support so that it could be lowered into the cryostat. All attempts to solder leads to the specimen failed and because of the extreme brittleness of the material it was possible to have only two pointed pressure contacts on the specimen. These were satisfactory at room temperature but became very erratic when cooled.

This meant that it was very difficult to measure the resistance of the specimen at liquid hydrogen temperatures making an accurate determination of the transition curbe impossible. It was, however, possible to see a definite reduction in potential across the specimen over a range of about $\frac{1}{2}^{o}$ at about 15°K which was both reproducible and reversible. For this experiment the large helium pumping system was used with a mercury manometer for temperature measurement and a temperature of about 10°K with a pressure of 2mm. of mercury above the solid hydrogen was obtained. Both control and measurement of the temperature proved to be very satisfactory.

Since even the largest piece of columbium nitride was less than $\frac{1}{2}$ cm. across and was not plane it was almost impossible to construct a sample suitable for reflection measurements and no reflectivity results were obtained.

Chapter 7

The results for the resistivity of copper, tin and silver shown in fig. 16, 17, 18, were obtained only as an auxiliary experiment and no attempt was made to investigate any unexpected phenomena for their own sake. This was especially the case as the only graph used was that for silver and it is the other two which show departures from linearity. The curve for silver agrees with the published results to well within the experimental error and is linear within the range of scatter so that no comment is required. The curves for copper and tin both show departures from linearity. As no trace has been found of similiar continuous measurements over this temperature range, comparison with other results is unsatisfactory. In the case of copper the effect consists of a break in slope centred at about 120°K after which the curve seems to settle down again to a steady slope less than that of the upper portion. The upper slope is o.57 $.10^{-8}$ ohm. cm./degree and the lower 0.32 $.10^{-8}$ ohm. cm./degree. Any mechanism accounting for this must be one which limits the conductivity, preventing the resistance from falling off as quickly as it ought. The mean free path of the conduction electrons at this temperature is about 2.10^{-5} cm. suggesting that this limitation of conductivity may arise from interaction between the electrons and lattice dislocations which would have approximately this spacing assuming a density of dislocations of 10^{10} /cm.^{2} This is not an unreasonable figure for material of this type and extra limitation of conductivity is to be expected when the mean free path of the electrons exceeds this spacing. However, it is not clear that this would have a continuous effect and would not merely result in a constant addition to the resistance following Matthiessen's law. The initial decrease in resistivity, too, is difficult to explain. In the case of tin, since only one point shows any divergence from the straight line, it is impossible to draw any conclusions. However, since this appears only in the specimen which was drawn down, it may be that a

process similiar to that suggested for copper may be taking place.

Work on the reflectivity and other optical properties of metals has in the past been concentrated on the variation of these properties with the wave-length of the incident radiation. This has been so because the rate of variation with wave-length is usually quite large while it was found that the effect of temperature was, if it existed at all, was extremely small. Experiments were done at temperatures higher than room temperature as there exists here a very convenient method of studying the optical properties in the near infra-red where the emissivity can be more accurately measured than the reflectivity. Temperatures lower than room temperature were used by Rayleigh (1930) and de Selincourt (1925) in studying the minimum in the ultra-violet reflectivity of silver but concluded that no effect existed other than a small change which could have been due to the small alteration of the lattice binding energy,

On the basis of the Maxwell theory the reflectivity is temperature dependent to the extent of varying as the square root of the conductivity of the metal but the assumptions inherent in the derivation of the Drude formula restrict the validity of this result to wave-lengths beyond the middle infra-red. At higher frequencies the behaviour of the electrons under an alternating electric field come more and more under the influence of inertial effects and the temperature becomes correspondingly less important. By the time, therefore, that the visible region is reached, the reflectivity is governed almost entirely by relaxation and the effect of temperature, although finite, is very small. It was this expectation, coupled with the experimental fact that the temperature variation was, indeed, below the limit of detection that diverted attention to the wave-length variation. However, it must not be overlooked that the theory which ought to take into account all resistive and inertial effects does predict a temperature variation which would be

observable and gives a value for the absolute reflectivity which is much higher than is observed.

The explanation frequently given that the effect is due to a surface layer of high resistivity really begs the question as no explanation is provided of the existence of this layer under circumstances such as an electrolytically polished or a high temperature emitting surface where it should not appear. It seems, therefore, that the considerations of the pure electron gas theory given in Chapter 2 are incomplete in some respect. We have taken into consideration the mass of the electrons and resistive damping on the assumption that it follows the same model as the d.c. conductivity. Any refinement of the theory has two methods of approach available. The factor which is giving rise to the anomalously high absorption can be connected with the high frequency of the radiation for the amplitude of the vibration of the electron is extremely small and the period much less than the mean free time so that it may be unjustifiable to assume that the d.c. conduction model is still valid. On the other hand we are dealing with a purely surface effect as the penetration depth of the radiation fields may be about 10^{-5} cm. It may be, therefore, that some mechanism related only to the behaviour of the electrons at the surface of the metal could limit the reflectivity.

It is the latter approach which has been used in the theory of Reuter and Sondheimer (1948). It had been postulated by London (1940) in the early work on the radio frequency resistance of tin that the anomalously high resistance observed by him was the result of the mean free path of the conduction electrons becoming comparable in length with the penetration depth of the radiation fields. This means that, for part of its course at least, an electron reflected from the surface of the metal is moving in a field smaller than the full radiation field and this is equivalent to an increase in observed resistivity. The effect is most marked at low temperatures and high wave-lengths where the conditions

are correct to give the greatest disparity between the two quantities. At higher temperatures where the mean free path is shorter the effect will become apparent at shorter wave-lengths where the penetration depth is less and the magnitude of the effect will decrease as the conditions are governed more and more by relaxation. The temperature for silver for which the penetration depth in the visible region and the electronic mean free path are equal turns out to be about 200° K. It is thus apparent that, if temperatures down to 20° K were available, the most profitable wave-length range would be the visible and the fact that the observed curves of reflectivity against temperature do show a minimum suggests comparison with the theory of Reuter and Sondheimer.

Before any detailed calculations can be attempted the validity of the various formulae available must be investigated. The results for the optical constants which are commonly used and were derived in chapter 2 are: -

$$n^2 - k^2 = 1 - (4\,ne^2)/m^2$$

$$2nk = (4\,ne^2)/m$$

But it was pointed out at the time that the assumptions inherent in the approximations used in deriving these render them invalid and, for the case where T the amended treatment where only a fraction of the electrons experience a collision during one period should be appropriate. The values for $n^2 - k^2$ and $2nk$ for this case have been given as : -

$$n^2 - k^2 = 1 - (4\ ne^2/m\ )(1 - (1/\ )(\ /8-1))$$

$$2nk = (4\ ne^2)/m$$

These formulae give numerical results which are actually very little different from those derived from the normal equations but this second set of equations ought to hold up to the highest frequencies where 2nk becomes negligable and the region of ultra-violet transparency is reached. Now, for the conditions of temperature and wave-length under which the present results were obtained, ie. a wave-length of about 5000Å and a conductivity for silver of about

10^{-6} ohm^{-1}. cm.$^{-1}$, we find that τ/T is about 40. We are therefore well within the region governed by the high frequency conductivity and we can calculate n and k from the second set of equations above. Since we have the value of the d.c. conductivity and so of τ for each temperature we ought then to be able to calculate the whole curve for reflectivity against temperature which is predicted by the classical model. Since we have already decided that the Reuter and Sondheimer theory is applicable to the present conditions, we must, therefore, apply the correction given by Reuter and Sondheimer for the curves of reflecting power against temperature before comparing them with the observed curves. For a detailed check that we are dealing with the region in which anomalous effects can be expected we must compare the calculated values of the mean free path l and the penetration depth δ. If we define the penetration depth as λ/k so that it is the distance travelled by the wave in the metal before its amplitude is reduced to $1/e^{2\pi}$ of its value at the surface, we find, using values of k derived from the above formulae, $\delta \simeq l.10^{-5}$cm. It is interesting to note that the formula for the penetration depth derived from the phenomonological theory: -

$$\delta = \sqrt{\lambda c/\sigma}$$

(assuming the permeability of the medium to be unity) gives, for the same conditions, a penetration depth of 5.5 $.10^{-8}$ cm. This illustrates well the extent of the breakdown of the classical theory under conditions where the frequency of the radiation is too high to allow the electrons to dissipate the incident energy at the rate appropriate to d.c. conditions. The mean free path we obtain from the relation: -

$$l = \tau v$$

where v is the velocity of the electrons at the top of the Fermi distribution. From the known value of this energy this works out at 1.39 $.10^{8}$ cm./sec. giving $l = 0.61 \times 10^{-4}$ cm.

This calculation shows that the conditions are approximately those under which the anomalous skin effect shows up but we ought really to compare the pentration depth with the distance actually travelled by an electron during the period of the wave. Now we have mentioned that the mean free time of the electrons for a representative temperature is about 40 times the period of the radiation and, since we have already said that the mean free path and the penetration depth of the radiation were about equal, the distance travelled by the electron into the metal in one period of the wave will be only 1/40 approximately of the penetration depth. The magnitude of any anonalous effect is thus going to be very much reduced but the exponontial fall of field strength inside the metal ensures that, even over only 1/40 of the arbitrarily chosen penetration depth, there is sufficient variation of field strength to maintain the effect. The fact, too, that the electrons will, in general, be reflected from the surface of the metal at angles other than right angles will tend to reduce the magnitude of the anomalous resistance.

These elementary considerations are, however, fully covered by the Reuter and Sondheimer treatment of the problem and detailed predictions will be based on their theory. The result of their treatment for the optical region is a correction which is to be applied to the classical value of the absorptivity. This correction can be applied to the value of 2nk and n and k worked out from the normal value of $n^2 - k^2$ and the corrected value of 2nk. The use of the phenomenological equation for the reflectivity R: -

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

then gives the curve for the reflectivity as a function of temperature which takes into account all the established corrections.

The Reuter and Sondheimer theory provides the above-mentioned correction as the ratio of the anomalous skin resistance R to the classical skin resistance R_c.

This correction, given graphically against in fig. 2 of their paper, is dependent on the value of a parameter κ. This parameter is a measure of the ratio of the distance travelled by an electron during one period of the wave to the penetration depth of the radiation and so determines the magnitude of the effect. The determining factor is actually $\alpha/\omega\tau$ which, using the expression for κ given by Reuter and Sondheimer: -

$$\alpha = \frac{8\pi^2\omega e^2 m^2 v^2 l^3}{c^2 h^3}$$

where c is the velocity of light and h is Planck's constant, can be written: -

$$\frac{\alpha}{\omega\tau} = \frac{8\pi^2 h^2 \nu \sigma^2}{c^2 h^3 n^2 e^2}$$

We then find that the value for $\alpha/\omega\tau$ for the present conditions is about 30 and the curve corresponding to this value can be interpolated in the diagram.

The values of R/R_∞ obtained from this can now be applied to the absorption nk evaluated from the classical theory, the values of n and k determined and hence the reflectivity R for each temperature. It is clear, however, that, since the change in absorption over this temperature range which is given by Reuter and Sondheimer is only a factor of two approximately, it will be almost completely swamped by the classical temperature variation which amounts to a factor of about four and no minimum can result. The result of applying the anomalous skin effect corection to an absorption which is independent of temperature is shown as curve b in fig. 19. The actual values of the ordinates on this second curve are not significant as they depend on the particular classical absorptivity chosen. In this case the absorptivity was chosen so that, with the Reuter and Sondheimer correction, it gave the experimentally observed value quoted below.

We can now stop to examine the deficiences of the predictions of the theory as developed so far. We must first consider the actual values for

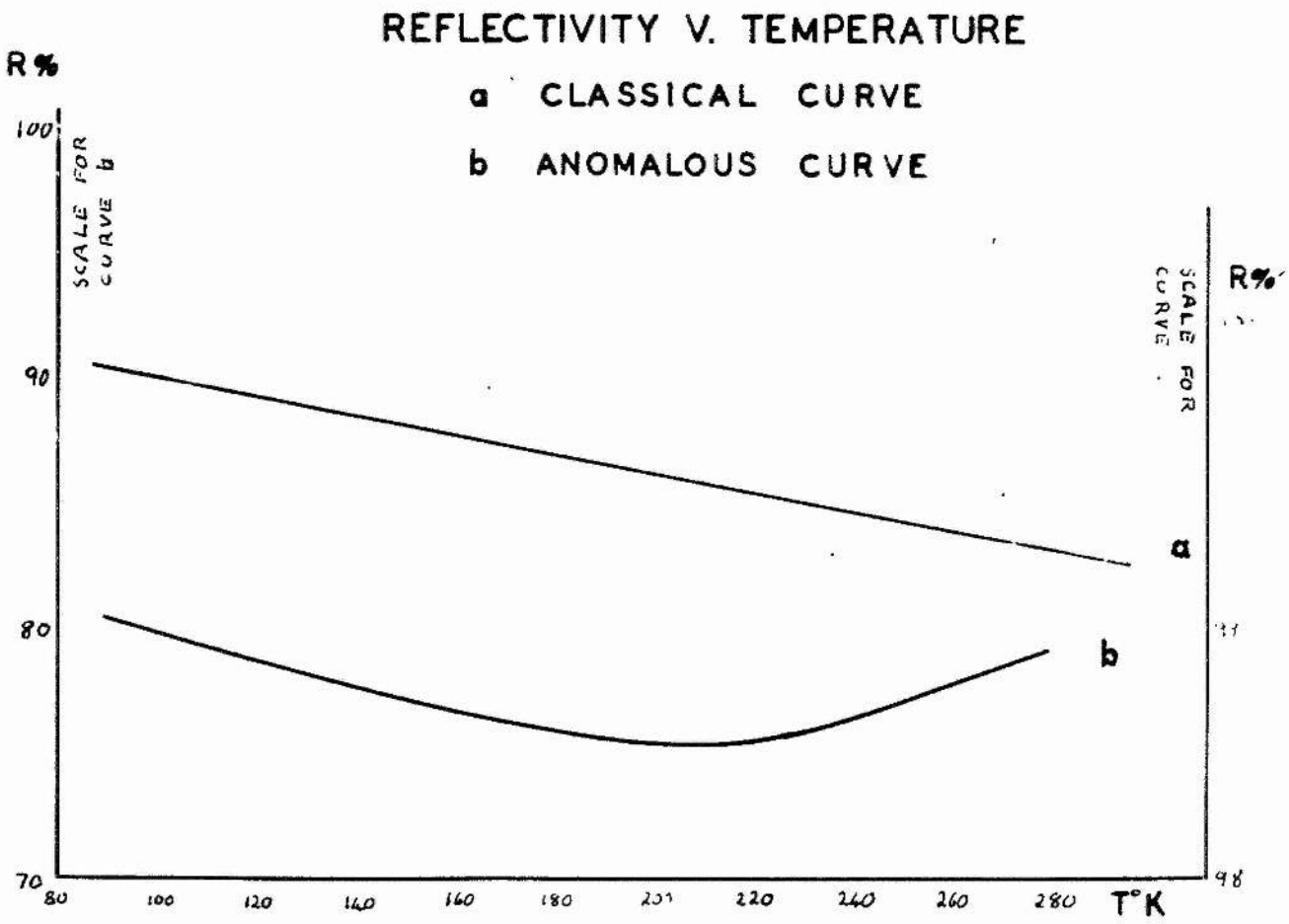

REFLECTIVITY V. TEMPERATURE
a CLASSICAL CURVE
b ANOMALOUS CURVE
R%
100
90
80
70
SCALE FOR CURVE b
SCALE FOR CURVE a
R%
a
b
80
100
120
140
160
180
220
240
260
280
T°K
98

Fig. 19.

n and k given by the electron gas model.

The results for silver obtained by Minor 1903 using the optical constants of reflected polarised light are n = .17 and k = 2.94 for a wave-length of 5000 A and room temperature. To facilitate comparison with the theoretical values we shall use $n^2 - k^2$ and 2nk and Minor's results give $n^2 - k^2 = -8,62$ and 2nk = 1.00. Minor's work was done before the importance of the method of surface preparation had been recognised and we may assume that the surfaces were mechanically polished. The experiments of Lowery and Moore (1932) on the effect of different polishing methods on the optical constants show that, in the case of copper, the absorption can be increased by any amount up to about 10% by mechanical polishing while the dielectric term remains almost unaltered. The increase in absorption, however, reaches this value only in the region of photoelectric absorption and, in the absence of any such effect in silver under the present conditions, we shall assume that Minor's results are not significantly in error.

In calculating $n^2 - k^2$ and 2nk from the electron gas formula, we must decide on the effective number of free electrons which we ought to use and care must be used as the experimentally determined values come normally from optical results. Chambers (1952) gives a result based on work on the anomalous skin effect at 2,500 Mc/s. This is admittedly very similiar to optical work but the formulation is different. He gives n = 0.61 and we then find that the calculated values of $n^2 - k^2$ and 2nk are $n^2 - k^2 = -8.605$ and 2nk = 0.0577. This means that almost perfect agreement between the theoretical and observed values is obtained for the dielectric term as it can be seen that the Reuter and Sondheimer correction to the reactance as shown in fig. 3 of their paper is negligable for the present conditions. In the case of the absorption, the experimental results should be examined for remaining deficiencies in the theory only after the Reuter and Sondheimer correction

has been applied. For room temperature, this correction may amount to a factor of 1.25. This gives a predicted absorption of 0.072 and we are thus left with a factor of 1/4 between the observed and predicted values of 2nk.

Turning to the temperature variation of reflectivity given by the present results we see that the shape of the curve is similiar to that which could be derived from the Reuter and Sondheimer absorption. An attempt to fit a Reuter and Sondheimer curve with an $\omega\tau$ value of about 30 to the present results shows that a similiar variation is obtained only if two conditions are fulfilled. Firstly, it can be seen that the application of the Reuter and Sondheimer correction to the classical variation of reflectivity as in curve a of fig. 19 cannot lead to a minimum as it is completely swamped by the temperature variation and ~~cannot lead to a minimum~~ gives only a slight change in slope. The curve obtained bears no resemblance to the observed one and the correspondance becomes satisfactory only if the correction is applied to an absorption which is almost constant with temperature as in curve b of fig. 19. Secondly, in order to obtain a minimum of reflectivity at the observed temperature, the value of $\omega\tau$ requires to be adjusted. The value of $\omega\tau$ calculated for the experimental conditions at the observed minimum is about 177 while, for the appropriate value of $\omega\tau$, the maximum in absorptivity is given by the Reuter and Sondheimer curve at a value $\omega\tau$ of about 8.

The probability that we are dealing with a maximum in absorptivity arising from interaction between the electronic mean free path and the penetration depth of the radiation fields can follow from the way in which the temperature of the reflectivity minimum depends on the wave-length. If we make the assumption that the effect is governed by the relative magnitudes of the mean free path and the radiation penetration depth we can examine the conditions under which they are of comparable magnitude.

Put $n^2 - k^2 = a$

$2nk = b$

so that $k = \sqrt{\frac{-a + \sqrt{a^2 + b^2}}{2}}$

The penetration depth $\delta = \lambda/k$ is then

$$= \frac{\sqrt{2}\ \lambda}{\sqrt{-a \pm \sqrt{a^2+b^2}}}$$

Assume that this is equal to a constant f times the mean free path $l = v\tau$

Thus $$\frac{\sqrt{2}\ \lambda}{\sqrt{-a^2 \pm \sqrt{a^2+b^2}}} = f v \tau$$

which gives $b = (4\lambda^2)/v^4\tau^4 f^2 + (4\lambda^2 a)/v^2\tau^2 f^2$

and since b is about .06 and $\lambda/v\tau$ about 10 we can neglect b compared with the right hand side of this equation giving

$$\lambda^2/v^2\tau^2 f^2 + a = 0$$

$$\frac{\lambda^2 n^2 e^4}{f^2 v^2 m^2 \sigma^2} = \frac{4\pi ne^2}{m\omega^2} = -1$$

$$= \frac{4\pi^2 ne^2\lambda^2}{4\pi^2 mc^2} = -1$$

Thus $1/\lambda^2 = K_1 (1/\sigma^2) + K_2$ where K_1 and K_2 are constants.

We see from this result that a plot of the inverse square of the wave-length against the inverse square of the conductivity at the temperature at which the reflectivity minimum for that wave-length occurs ought to give a straight line, the slope of which will give the ratio of the penetration depth to the mean free path at the reflectivity minimum. Table 1 gives the relevant data on the wave-lengths and conductivities involved.

Table I

λ	T_{min}	$\sigma \times 10^6$ ohm^{-1}cm^{-1}	$\frac{1}{\sigma^2} \times 10^{12}$	$\frac{1}{\lambda^2} \times 10^{10}$
0.4700	237	0.790	1.602	4.527
0.5225	228	0.830	1.453	3.663
0.5900	219	0.868	1.329	2.873
0.6800	210	0.941	1.113	2.163
0.9300	175	1.122	0.810	1.235

$1/\lambda^2$ and $1/\sigma^2$ are plotted in fig. 20. It appears that, within the limits of scatter, the curve is a straight line which has a slope of $3.34 \cdot 10^{44}$ (e.s.u. conductivity units)^2 /cm^2. The slope evaluated from the equation between $1/\lambda^2$ and $1/\sigma^2$ is $43/f^2 \cdot 10^{44}$ so that f must be 3.6. This can be compared with the rough estimate made before the calculations were started which made the ratio between the penetration depth and the mean free path about 3. It seems, therefore, that the interpretation of the results in the light of the Reuter and Sondheimer effect is at least consistent.

The discrepancies still requiring explanation are firstly, that the basic absorption, before the Reuter and Sondheimer correction is applied, seems to be independent of the temperature while the absorption predicted by the simple electron gas theory undergoes a fourfold change in accordance with the conductivity change over the present temperature range. Secondly, while the predicted value of the dielectric term $n^2 - k^2$ agrees extremely well with that observed, there is a discrepancy between the calculated and observed values of 2nk of a factor of about 14 and between the values of $\omega\tau$ referring to the minimum of reflectivity in the temperature variation of about 22. Although the numerical agreement between those two factors is not perfect, it may be argued that, considering the uncertainty of absorption measurements, the correspondance is sufficiently close to justify the assumption that the same quantity is giving rise to both discrepancies. The only possible quantities are ω and τ and the agreement obtained in the case of $n^2 - k^2$ which involves ω only indicates that it is the mean free time τ which is the source of the disagreement.

This is merely another way of stating the often quoted fact that the optical properties seem to be governed by a resistance which is about ten times the observed d.c. resistance. However, the above argument shows that the discrepancy is not restricted to the absorption but is shown up consistently

1/(CONDUCTIVITY)^2 V. 1/(WAVE-LENGTH)^2
SILVER

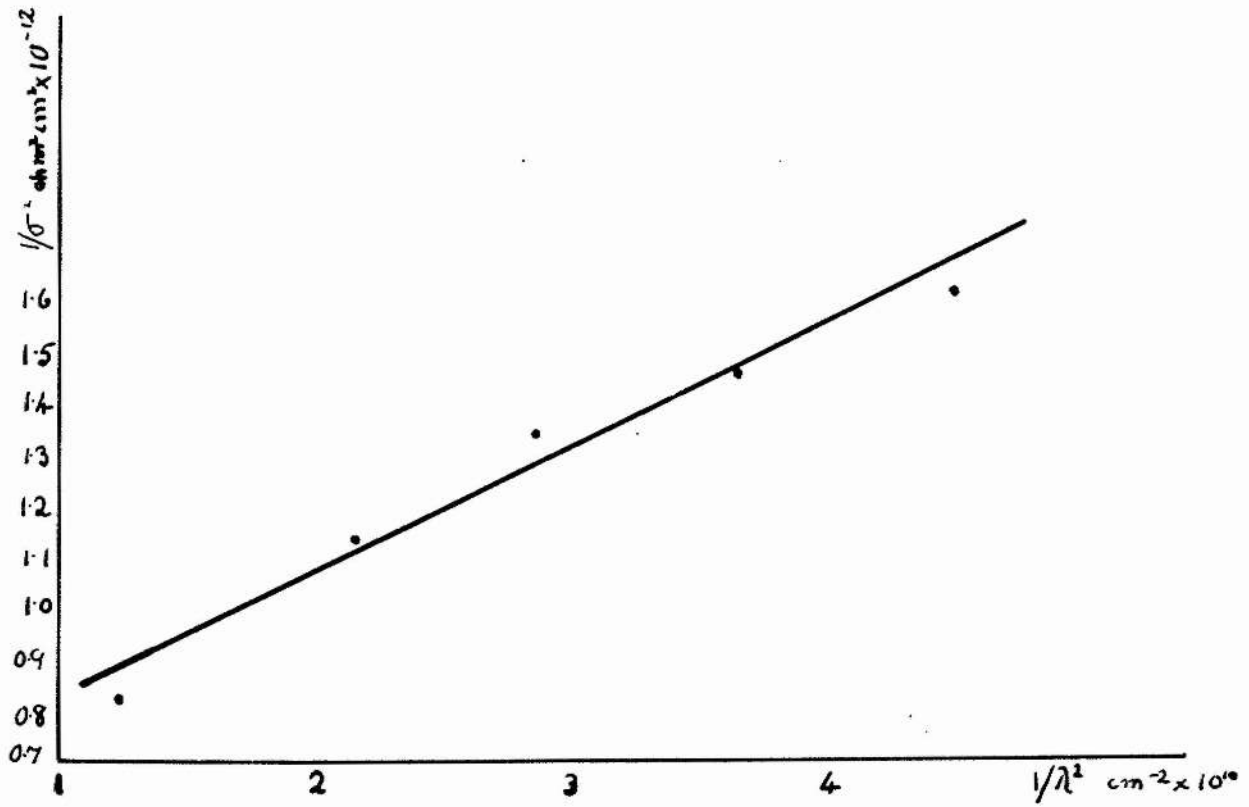


Fig. 20.

in other approaches to the problem which may indicate that the phenomenon is of rather more significance than has been previously admitted. In any case there are many objections to the suggestion that the high absorption is due merely to a surface layer of high resistance. For, if this layer had been formed by polishing, it should have no effect on the results obtained from the high temperature emissivity of metals where no stresses can remain in the surface and the discrepancy could be removed simply by electrolytic polishing. Also a simple increase in resistivity should have just as much effect on the infra-red reflectivity and would make it difficult to explain the fact that the divergence found by Hagen and Rubens between their results and the Drude formula is less than .1%.

The results of Reid (1941) on the reflectivity of nickel at temperatures up to 900° C show that the Drude relation is obeyed for wave-lengths above 5μ and the reflectivity then falls below the predicted value reaching a minimum at 1μ. This does not sound like the behaviour resulting from the addition of a constant skin resistance superimposed on the thermal resistance which is commonly proposed and it is typical of results obtained under those conditions. The measurements of Hurst (1933) on the emissivity of copper and nickel at temperatures up to 850° C and wave-lengths up to 5μ show that, while the Drude relation is not obeyed exactly in this region, the correspondence with the Kronig theory (which, in the absence of photoelectric absorption, gives substantially the same results as the classical electron gas theory) is even worse. The experiments of Price (1947) on the emissivity of a number of metals confirm Hurst's results and also a similiar effect found by McCauley (1913) in platinum but do not clarify the situation to any extent. The only other important experiments are those of Ramanathan (1952) on the reflectivity of metals in the infra-red at low temperatures. The aim was primarily the study of the change in optical properties at the superconducting

transition and radiation of about 10μ wave-length was used. No effect was detectable at the transition but the absorption for normal metals was higher than was expected and agreement with the Reuter and Sondheimer theory was obtained only by ignoring relaxation effects which seems unreasonable [redacted] or by the assumption of an anomalously high skin resistance.

The high temperature measurements have been stressed because it is only there that the departure from the predictions of the phenomenological theory comes at a conveniently high frequency. The electron gas theory seems to give reasonable agreement for frequencies well below $1/\tau$ and later, of course, tends to the same value as the phenomenological theory. The common feature of the experiments mentioned above is, therefore, that the divergencies all become apparent at wave-lengths and temperatures at which is about equal to $1/\tau$ (This is equivalent to the distinction drawn by Hurst [redacted] and Weniger and Pfund [redacted] between "electrical" and "optical" properties. This is the region which, as was pointed out earlier, cannot be treated by the simple electron gas methods used for the other frequency ranges and in which no predictions could be made. However, the anomalies extend to wave-lengths in the visible where the theory outlined for the case where T is less than τ is applicable. It appears, then, that the model used in that treatment is deficient in some respect.

It would be well to recall the precise nature of this model and the assumptions made in the development. The electron was considered to be free, moving with a velocity appropriate to the top of the Fermi distribution. The remaining factor specifying the motion of the electron was taken to be a mean free path between collisions with the lattice, this mean free path being derived from a mean free time which governs the d.c. conductivity. We then assumed that each electron would react in a classical fashion to any alternating electric

field and the use of a damping coefficient m/τ implies the assumption that the damping is behaving in the same way as the d.c. resistance. The electrons were assumed to re-emit independently and to move in spatially uniform electric fields. Ignoring other deficiences such as the assumption that $\underline{P}$ and $\underline{E}$ are parallel which, in the presence of resistance, is not the case, the neglect of the polarisation of the inner electron shells which makes only a small contribution to the total polarisation for visible and infra-red wave-lengths and of the Lorentz force on the electrons, due to the magnetic component of the incoming radiation, which is generally regarded as negligible, we are left with the above considerations in the search for the source of the discrepancy.

The spatial variation of the radiation fields is the effect considered by Reuter and Sondheimer but it is apparent that their correction is not sufficient to explain the whole discrepancy. The acceleration part of the model is not likely to be the cause for, although it would be difficult to justify the application of a classical acceleration to an electron which is subject to wave mechanical considerations in its interaction with the lattice, the agreement obtained between the predicted and observed wave-lengths for the onset of ultra-violet transparency of the alkali metals demonstrates that the acceleration part of the equation is satisfactory. The deficiencies of the assumption concerning independent scattering are shown by the application of the treatment commonly used in the theory of X-ray scattering. The rate of emission of energy from an accelerated charge e is well known to be :-

$$P = (2/3)(e^2a^2)/c^3$$

where a is the acceleration of the charge. If the acceleration is caused by a periodic electric field $\underline{E} = E\,e$ then:-

$$P = (2/3)(e^4E^2)/m^2c^3$$

where m is the mass of the charged particle. The incident energy flux per

square centimetre is $cE^2/4\pi$ and so the ratio of the re-emitted energy flux to the incident flux is :-

$$R = (8\pi/3)e^4/m^2c^4$$

If we now assume that all the n electrons in each cubic centimetre of the metal experience the full incident wave intensity and that all the re-emitted radiation is concentrated into one direction to constitute a reflected beam, R should be a measure, under the most favourable circumstances, of the reflectivity of the system. However, an evaluation of the above quantity gives R about 4% so that the electrons, acting under those conditions, are incapable of re-emitting sufficient to provide the reflecting power. It would appear, therefore, that the assumption of independent scattering, which is made in all electron gas theories of optical phenomena, is hardly justifiable but the development of a theory of coherent scattering would be very difficult.

The only other possibility apparent is in the structure of the model itself. This relied on the assumption that the motion of the electron consisted of periods of free motion with the Fermi energy terminated by scattering to another direction with substantially the same energy. It might be argued, then, that the origin of the anamolous absorption is merely a misinterpretation of the nature of the mean free time. It is commonly pointed out that the mean free path is most logically introduced through the relaxation time which is defined in terms of the rate of change of a disturbed electron distribution. There is nothing in this definition to indicate that the distance travelled by an electron in this relaxation time should be regarded as completely "free". While it may take this time or distance to effect any large-scale change in the conditions, the presence of resistive damping along this path need not be precluded. The fact that Hurst states that the Drude formula fits his results better than the Kronig theory and that the absorption in the visible is

diverging from the electron gas theory in the direction of the Maxwell prediction suggests that the tendency of the behaviour in this region is towards that predicted by a smoothed conductivity. Without a detailed study of the resistance mechanisms, it would be difficult to make detailed predictions regarding the optical behaviour and it is not clear why this should give the constant effective resistivity which the virtually constant absorption requires. It would be difficult to obtain further information from other experimental results for, with the possible exception of resistivity size effects at low temperatures, it is only in the optical behaviour in this wave-length region between the onset of transparency and the resistance controlled region that any microstructure in the resistance would be apparent.

So far we have considered only the volume effects. The surface effects are fairly fully covered by the Reuter and Sondheimer theory which has already been discussed and shown to leave a residual discrepancy unexplained. Their treatment has been extended by Dingle (1952) who has given solutions of the equations leading to the surface impedance in the optical region. He has considered both cases when the reflection of electrons from the surface is diffuse and when it is specular and finds that, for specular reflection, no further absorption of energy will take place but, for diffuse reflection, the surface resistance is increased by a factor $1 + \frac{1}{4}(3\kappa/\omega\tau)^{\frac{1}{2}}$. It appears to be generally accepted (Chambers 1952) that the assumption of diffuse reflection is the more appropriate so that Dingle's correction should be valid. In comparison with the results of Forsterling and Freedericksz (1913) and of Ramanathan (1952) reasonable agreement is reached. These results, however, refer only to the near infra-red and a calculation of the correction for the present conditions gives a factor of about five in the absorption. As the original discrepancy between predicted and observed values was a factor of about 14, a factor of about three or four in the absorption remains unexplained.

A method given by Holstein (1952) also predicts enhanced absorption in the case of diffuse reflection and, although his result has the merit that the absorption obtained is independent of temperature, in absolute magnitude it is far too low, being, in the case of silver, about .5%. His argument is that, even in the absence of resistive damping, energy would be absorbed from the radiation fields, and, while this must obviously be the case, it is claimed that detailed calculations show that, whatever the actual values, the energy absorbed in the case of diffuse reflection is much higher than for specular reflection. His treatment is based on the difference in absorption between the two parts of an electron's path through the penetration depth before and after scattering at the surface. Because of the random nature of the scattering these will not be symmetrical about the normal at the point of scattering and this is claimed to lead to an increased absorption. However, the energy carried out of the radiation field by an electron must be very small under the present conditions since the time taken to traverse the whole path is of the order of 100 wave periods. Also the distinction between the specular and diffuse reflections for this purpose is not clear physically as, even if an electron is reflected with an arbitrary velocity, it would be possible, considering the number of electrons involved and the random nature of the reflection, to associate the electrons in such a way that the reflected velocity of each fitted the incident velocity of another so that the system would not be distinguishable by the radiation field from a set of specular reflections.

The above discussion has been devoted solely to silver on account of the simpler nature of the results and the absence of any obvious complicating factors. In the case of copper the circumstances must be similiar to those for silver except for the presence of the photoelectric absorption band at the short wave-length end of the visible spectrum. This means that, for wave-lengths

greater than about 5,000 A, the absorption will be much greater than will be predicted on the basis of the free electron gas theory and comparison with the kronig treatment is required. However, even if we consider the red end of the spectrum as far away as possible from the influence of the photoelectric absorption, we find that the circumstances are similar to those for silver. The main difficulty in the case of copper lies in the evaluation of the effective number of free electrons per atom. In the present calculations the value obtained by Chambers (1952) has been used as it is more in accord with theoretical expectation. With n 2 1.01 we then find that for a wave-length of 6,000 A, $n^2 - k^2 = -27$ and $2nk = .38$ while the observed values are -9.22 and 3.5 respectively (Minor 1903). The discrepancy in $n^2 - k^2$ is merely that which has given rise to the conclusion that the optical properties of copper lead to a value of n of 0.37. The situation is usually explained in terms of the oxide layer which always forms on copper surfaces exposed to air. We can, however, see that the conditions are roughly the same as for silver. The shape of the temperature variation again suggests a Reuter and Sondheimer influence and we can probably assume that the same mechanisms as for silver are operative. One feature of additional interest is the disposition of the temperatures of the reflectivity minima for different wave-lengths. It can be seen that the effect of the photoelectric absorption is to move the minimum towards lower temperatures. This involves the assumption either that the penetration depth increases sharply towards the absorption region or that the mean free path, for the same temperature, has been reduced. The variation of the extinction coefficient over the whole wave-length range (Minor 1903) shows that the penetration depth should increase as the wave-length decreases but there is no sudden change as required by the present result. We are thus left with the supposition that the electronic free time effective for optical processes may be less in the photoelectric absorption band than it is outside it for

the same temperature. The mechanism of photoelectric absorption is not known precisely. The possible excitations are (a) from a low level in a conduction band to a higher level in the same band; (b) from a lower, filled, band to a conduction level. In the case of copper, the absorption edge at 5730A may be due to ionization of the 3d level which is the last filled band. It may be, then, that the possibility of a conduction electron dropping to the 3d level is equivalent to the existence of a finite electronic life time in the conduction band and this would reduce the free time available for optical processes. It would possibly be of interest to examine the case of zinc which has a photoelectric absorption band in the near infra-red. It would then be possible to approach the band from the other side to see if any comparable effect takes place in the opposite direction. The curves for copper are considerably less smooth than for silver but, considering the doubts attached to such results on grounds of surface effects etc. it is probably unjustifiable to draw any conclusions from any feature other than the general shape of the curves.

The results for tin are even more complicated by minor irregularities. The first point to be noted is that the wave-length dependence of reflectivity, although small, is the opposite of that of silver and copper in that the reflectivity increases slightly towards the blue end of the spectrum. The overall tendency found by Coblentz between the ultra-violet and the infra-red is for the reflectivity to increase in the normal way towards the red and so the change we have found within a limited wave-length range must be a minor divergence from the large scale variation. Secondly, although the same general features as before for copper and silver may be observed in the temperature variation, any minimum of reflectivity seems to be double. This would point to two separate n_{eff} values and this can be understood on the basis of the well known anisotropy

of the conductivity of tin. The maximum change in conductivity between two crystal orientations amounts to about 25% of the maximum value (Pippard 1950). A change of 25% in the conductivity under these conditions is equivalent to a temperature change of about 40°C which is not too remote from the separation of the minima which is observed.

Very little data are available for the optical properties of tin so that no comparison with other results is possible. Chambers (1952) gives the effective number of free electrons as 1.12 per atom so that the mean free time derived from the d.c. conductivity is not very different from that for silver. One absorption measurement (Erochin 1912) gives $k = 5.25$ for a wave-length of 5890 A so that the penetration depth is almost exactly 10^{-5} cm. The conditions are thus almost exactly the same as for copper and silver and, apart from considerations of anisotropy, we would expect very little difference in the reflectivity results from those the other metals.

In conclusion, we can say that the present results indicate that the anomalous skin effect can be observed at temperatures and wave-lengths higher than those at which it is normally studied. Since this effect, although much reduced from its low temperature magnitude, may persist to room temperatures, this helps to explain the anomalously high values of the absorptivity of metals which have always been found in the visible and near infra-red regions of the spectrum. A residual discrepancy, however, remains which is reduced but not eliminated by Dingle's treatment. It has been pointed out that the discrepancy is restricted to the region where $\omega \gg 1/\tau$ and, while the precise mechanism of the absorption process remains obscure, it has been suggested that the disagreement arises from the breakdown of the model which is used or assumed implicitly in this region and which involves a possible misinterpretation of the significance of the mean free time of the electrons.

Table II : Shutter Calibration

$a = 18$

x	$A(x) = 2\pi \int_0^x \sqrt{a^2 - (x-a)^2}\, dx$
2	2.225
4	6.186
6	11.146
8	16.842
10	23.076
12	29,705
14	36.636
16	43.704
18	50.884
20	58.084
22	65.152
24	72.083
26	78.712
28	84.947
30	90.642
32	95.603
34	99.563
36	101.736

Table III : Electrical Resistivity of Copper

T°K	Resistivity (ohm cm. 10^{-6})
77	0.276
81	0.280
86	0.280
91	0.312
97	0.332
101	0.353
107	0.355
112	0.399
117	0.433
122	0.468
126	0.501
130	0.530
134	0.576
138	0.613
143	0.624
147	0.645
150	0.682
154	0.694
158	0.713
162	0.738
166	0.754
170	0.774
173	0.796
177	0.825
181	0.841
184	0.861
187	0.872
190	0.890
193	0.914
197	0.927
200	0.946
203	0.960
206	0.984
210	0.990
213	1.013
216	1.032
219	1.047
222	1.065
225	1.093
228	1.105
231	1.119
234	1.137
237	1.149
239	1.168
242	1.190
245	1.200
248	1.220
251	1.242

Table III contd.

T°K	Resistivity (ohm cm. 10^{-6})
254	1.255
256	1.267
259	1.289
262	1.306
265	1.319
267	1.334
270	1.351
273	1.370

Table IV : Electrical Resistivity of Tin

	T°K	Resistivity (ohm cm. 10^{-6})				Average
A	91	1.891				
	117	2.631				
	140	3.426				
	160	4.117				
	180	4.657				
	197	5.202				
	213	5.732				
	229	6.268				
	244	6.803				
	258	7.183				
	273	7.663				
B	91	1.392	1.459	1.396	1.463	1.428
	117	1.915	1.978	1.995	1.995	1.971
	140	2.449	2.506	2.339	2.462	2.454
	160	2.793	2.901	2.866	2.932	2.873
	180	3.192	3.297	3.337	3.332	3.290
	197	3.722	3.693	3.673	3.737	3.706
	213	4.121	4.023	4.007	4.138	4.072
	229	4.450	4.419	4.416	4.405	4.421
	244	4.782	4.676	4.745	4.672	4.720
	258	5.054	5.071	5.083	5.075	5.071
	273	5.324	5.350	5.350	5.409	5.355
C	91	2.577	2.698	2.577		2.617
	117	4.141	4.683	4.733		4.519
	140	5.353	5.575	5.665		5.531
	160	6.163	6.284	6.332		6.260
	180	6.878	7.012	7.012		6.967
	197	7.526	7.679	7.559		7.588
	213	8.236	8.188	8.227		8.217
	229	8.828	8.704	8.643		8.725
	244	9.327	9.106	9.021		9.151
	258	9.889	9.546	9.374		9.603
	273	10.456	10.461	10.359		10.425

Table V : Electrical Resistivity of Silver

T°K	Resistivity (ohm cm. 10^{-6})
92	0.453
99	0.501
120	0.574
141	0.725
157	0.794
179	0.905
196	1.005
214	1.082
234	1.212
245	1.291
252	1.321
260	1.381
273	1.419

Table VI : Reflectivity of Copper λ = 4,700 A

T°K	Reflectivity	T°K	Reflectivity
24	1.1533	203	0.9527
32	1.1442	206	0.9758
44	1.1383	210	0.9918
53	1.1138	213	1.0000
63	1.1034	216	1.0083
7o	1.1092	219	1.0211
81	1.0824	222	1.0342
86	1.0561	225	1.0386
91	1.0500	228	1.0544
97	1.0062	231	1.0637
101	1.0364	234	1.0637
107	1.0544	237	1.0661
112	1.0614	239	1.0731
117	1.0661	242	1.0779
122	1.0755	245	1.0803
126	1.0521	248	1.0876
130	1.0499	251	1.0779
134	1.0386	254	1.0661
138	1.0342	256	1.0637
143	1.0297	259	1.0453
147	1.0386	262	1.0362
150	1.0341	265	1.0233
154	1.0211	267	1.0211
158	1.0041	270	1.0166
162	1.0041	273	1.0000
166	0.9979	279	0.9962
170	0.9719	290	0.9962
173	0.9603	300	0.9984
177	0.9508	307	0.9955
181	0.9416	318	0.9904
184	0.9325	324	0.9938
187	0.9307	336	0.9850
190	0.9343	343	0.9773
193	0.9272	349	0.9800
197	0.9343	356	0.9694
200	0.9453	369	0.9694

Table VII : Reflectivity of Copper λ = 5,225A

T°K	Reflectivity	T°K	Reflectivity
31	1.2339	216	1.1631
44	1.2292	219	1.1659
57	1.2121	222	1.1507
66	1.1806	225	1.1143
75	1.1610	228	1.1108
81	1.1403	231	1.0935
86	1.1416	234	1.0834
91	1.0985	237	1.0834
97	1.0892	239	1.0769
101	1.0892	242	1.0769
107	1.0754	245	1.0852
117	1.0446	248	1.0868
122	1.0511	251	1.0801
134	1.0356	254	1.0834
138	1.0388	256	1.0735
143	1.0356	259	1.0702
150	1.0236	262	1.0687
154	1.0542	265	1.0654
158	1.0449	267	1.0517
162	1.0818	270	1.0542
166	1.0834	273	1.0511
170	1.0868	284	1.0708
173	1.0986	290	1.0810
177	1.1178	295	1.0836
181	1.1395	300	1.0887
184	1.1582	307	1.0861
187	1.1815	311	1.0887
190	1.1856	318	1.0861
193	1.1896	324	1.0861
197	1.1815	343	1.0810
200	1.1856	349	1.0658
203	1.1815	356	1.0658
206	1.1856	362	1.0658
210	1.1776	369	1.0484
213	1.1737		

Table VIII : Reflectivity of Copper λ = 5,900 A

T°K	Reflectivity	T°K	Reflectivity
42	1.7424	210	1.3551
52	1.7060	213	1.3609
60	1.6945	216	1.3609
65	1.6623	219	1.3609
70	1.6285	222	1.3805
75	1.6176	225	1.3965
81	1.5700	228	1.4192
86	1.5674	231	1.4341
91	1.5648	234	1.4384
97	1.5648	237	1.4491
101	1.5855	239	1.4602
107	1.6013	242	1.4827
112	1.6067	245	1.4827
117	1.6122	248	1.4966
122	1.6067	251	1.5106
126	1.6041	254	1.5154
130	1.5649	256	1.5323
134	1.5497	259	1.5447
143	1.5398	262	1.5648
147	1.5203	265	1.5751
150	1.4873	267	1.5726
154	1.4514	270	1.5777
158	1.4427	273	1.5988
162	1.4470	279	1.6309
166	1.4470	284	1.5988
170	1.4491	290	1.5863
173	1.4427	307	1.5863
177	1.4341	311	1.5771
181	1.4088	324	1.5470
184	1.3570	330	1.5679
187	1.3534	343	1.5679
190	1.3418	349	1.5590
193	1.3418	356	1.5560
197	1.3418	362	1.5560
200	1.3420	369	1.5500
206	1.3513		

Table IX : Reflectivity of Copper λ = 6,800 A

T°K	Reflectivity	T°K	Reflectivity
27	1.8837	208	1.5822
50	1.8775	211	1.6076
62	1.8597	215	1.6076
67	1.8328	218	1.5948
72	1.8116	221	1.6076
80	1.7968	224	1.6142
86	1.7341	227	1.6275
91	1.7147	230	1.6375
96	1.7303	233	1.6410
102	1.6898	236	1.6512
106	1.6253	239	1.6649
112	1.5273	242	1.6792
117	1.4900	244	1.7044
122	1.4466	247	1.7265
127	1.4466	250	1.7456
131	1.4681	253	1.7610
135	1.4818	256	1.7571
139	1.4884	259	1.7648
143	1.4872	261	1.7571
145	1.4762	264	1.7728
152	1.4789	267	1.7494
155	1.4985	270	1.7571
159	1.4985	273	1.7571
163	1.5127	284	1.7290
167	1.5243	290	1.7018
171	1.5391	295	1.6951
175	1.5333	300	1.6657
178	1.5333	311	1.6657
182	1.5215	324	1.6754
186	1.5333	336	1.6624
189	1.5215	343	1.6624
192	1.5482	349	1.6592
195	1.5333	356	1.6497
198	1.5421	362	1.6436
202	1.5571	369	1.6436
205	1.5633		

Table X : Reflectivity of Tin λ = 4,700A

T°K	Reflectivity	T°K	Reflectivity
35	0.9952	210	1.0206
46	0.9681	213	1.0206
50	0.9548	216	1.0378
63	0.9402	219	1.0378
79	0.9309	222	1.0378
85	0.9204	225	1.0421
98	0.9110	228	1.0248
112	0.9114	231	0.9801
117	0.9148	234	0.9840
122	0.9148	237	0.9573
126	0.9148	239	0.9762
134	0.9648	242	0.9648
138	0.9536	245	0.9610
143	0.9686	248	0.9686
147	0.9762	251	0.9648
150	0.9500	254	0.9686
154	0.9285	256	0.9648
158	0.8981	259	0.9081
162	0.8949	262	0.9724
166	0.9014	265	0.9801
170	0.8949	267	0.9880
177	0.9285	270	0.9919
181	0.9391	273	1.0000
184	0.9469	290	0.9879
187	0.9391	300	0.9825
193	0.9500	310	0.9581
197	0.9724	324	0.9482
200	0.9762	334	0.9433
203	0.9959	349	0.9433
206	1.0040	369	0.9384

Table XI : Reflectivity of Tin λ = 5,225A

T°K	Reflectivity	T°K	Reflectivity
41	0.8613	213	0.8508
46	0.8843	216	0.8441
59	0.8646	219	0.8508
72	0.8548	222	0.8508
77	0.8423	228	0.8575
93	0.8416	231	0.8643
101	0.8643	234	0.8818
107	0.8441	237	0.8854
117	0.8782	239	0.9076
122	0.8713	242	0.9000
130	0.8963	245	0.9000
134	0.8747	248	0.9112
138	0.8508	251	0.9190
143	0.8575	254	0.9269
147	0.8609	256	0.9308
150	0.8542	259	0.9151
154	0.8643	262	0.8891
162	0.8854	265	0.8995
166	0.8818	267	0.8441
170	0.8475	270	0.8441
173	0.8609	273	0.8411
177	0.8475	279	0.8292
181	0.8409	284	0.8121
184	0.8409	311	0.7903
187	0.8409	318	0.7798
193	0.8409	324	0.7824
197	0.8377	330	0.7747
200	0.8409	336	0.7696
203	0.8441	343	0.7696
206	0.8409	349	0.7696
210	0.8441	356	0.7646

Table XII : Reflectivity of Tin λ = 5,900 A

T°K	Reflectivity	T°K	Reflectivity
44	0.8083	216	0.8673
49	0.7973	219	0.8673
60	0.7933	222	0.8801
64	0.7936	225	0.8880
73	0.7754	228	0.8801
80	0.7612	231	0.8724
91	0.7610	234	0.8776
97	0.7572	237	0.8673
101	0.7650	239	0.8673
107	0.7553	242	0.8648
112	0.8288	245	0.8749
117	0.8381	248	0.8776
122	0.8525	251	0.8673
126	0.8673	254	0.8624
130	0.8724	256	0.8525
134	0.8724	259	0.8405
138	0.8648	262	0.8623
143	0.8598	265	0.8452
147	0.8476	267	0.8405
150	0.8500	270	0.8334
154	0.8500	273	0.8288
158	0.8500	279	0.8266
162	0.8374	284	0.8626
166	0.8623	290	0.8233
170	0.8648	295	0.8179
173	0.8476	300	0.8201
177	0.8175	307	0.8179
181	0.8175	311	0.8201
184	0.7977	318	0.8223
187	0.8021	324	0.8201
190	0.7977	334	0.8179
193	0.8021	344	0.8201
200	0.8265	352	0.8162
203	0.8288	362	0.8162
206	0.8334	370	0.8179
210	0.8598	373	0.8143
213	0.8724		

Table XIII : Reflectivity of Tin λ = 6,800 A

T°K	Reflectivity	T°K	Reflectivity
37	0.7345	213	0.7404
39	0.7409	216	0.7339
46	0.7252	222	0.7540
62	0.7262	225	0.7588
66	0.7242	228	0.7565
81	0.7347	231	0.7518
90	0.7450	234	0.7540
97	0.7565	237	0.7495
98	0.7612	239	0.7472
101	0.7612	242	0.7495
107	0.7565	245	0.7450
112	0.7427	248	0.7495
117	0.7427	251	0.7495
122	0.7612	254	0.7450
130	0.7572	256	0.7518
137	0.7578	259	0.7612
143	0.7588	262	0.7636
147	0.7565	265	0.7659
150	0.7565	267	0.7707
154	0.7540	270	0.7756
158	0.4772	273	0.7732
162	0.7518	284	0.7808
166	0.7472	295	0.7770
170	0.7540	300	0.7620
173	0.7588	307	0.7548
181	0.7565	311	0.7548
184	0.7565	318	0.7271
187	0.7588	324	0.7304
190	0.7450	330	0.7205
193	0.7404	336	0.7238
197	0.7360	343	0.7238
200	0.7383	349	0.7238
203	0.7360	356	0.7238
206	0.7330	362	0.7238
210	0.7383	369	0.7205

Table XIV : Reflectivity of Silver = 4,700 A

T°K	Reflectivity	T°K	Reflectivity
25	0.9493	190	0.9549
36	0.9385	193	0.9424
50	0.9187	197	0.9231
66	0.9241	200	0.9137
75	0.9278	203	0.9045
81	0.9375	206	0.8978
86	0.9302	210	0.8867
91	0.9756	213	0.8802
97	0.9890	216	0.8674
101	0.9890	219	0.8845
107	1.0000	222	0.8933
112	1.0256	225	0.8933
117	1.0285	228	0.8780
122	1.0465	231	0.8612
126	1.0405	234	0.8431
130	1.0315	237	0.8238
134	0.9945	239	0.8372
138	0.9945	242	0.9254
143	0.9890	245	0.9523
147	0.9890	248	0.9730
150	0.9890	251	0.9890
154	0.9890	254	0.9836
158	0.9890	256	0.9836
162	0.9890	259	0.9836
166	0.9703	262	0.9863
173	0.9809	265	0.9917
177	0.9231	267	0.9944
181	0.9424	270	1.0000
184	0.9375	273	1.0000
187	0.9498		

Table XV : Reflectivity of Silver λ = 5,225 A

T° K	Reflectivity	T° K	Reflectivity
46	1.1753	200	1.1660
58	1.1785	203	1.1478
65	1.1660	206	1.1418
70	1.1583	210	1.1302
75	1.1538	213	1.1360
81	1.1614	216	1.1390
86	1.1691	219	1.1390
91	1.1691	222	1.1020
97	1.1753	225	1.0857
101	1.1847	228	1.0752
107	1.1976	231	1.0830
112	1.2553	234	1.0911
117	1.2626	237	1.1103
134	1.2964	239	1.1188
138	1.2646	242	1.1390
143	1.2435	245	1.1449
147	1.2435	248	1.1628
150	1.2529	251	1.1753
154	1.2341	254	1.1879
158	1.2035	256	1.1910
162	1.1777	259	1.1721
166	1.1706	262	1.1815
170	1.1600	265	1.1753
173	1.1588	267	1.1721
182	1.1684	270	1.1815
197	1.1753	273	1.1753

Table XVI : Reflectivity of Silver λ = 5,900 A

T°K	Reflectivity	T°K	Reflectivity
46	1.4650	177	1.5777
58	1.4611	181	1.5868
65	1.4766	184	1.5733
70	1.4806	187	1.5256
75	1.4806	190	1.5006
81	1.4806	200	1.4570
86	1.4846	203	1.4380
91	1.5089	206	1.4231
97	1.5130	210	1.4049
101	1.5513	213	1.3800
107	1.5688	216	1.3766
112	1.5777	219	1.3395
117	1.5823	222	1.3529
122	1.5688	225	1.3698
126	1.6145	228	1.4231
130	1.6336	231	1.4418
134	1.6481	234	1.4687
138	1.6579	237	1.4493
143	1.6287	239	1.4687
147	1.6239	242	1.4570
150	1.6192	256	1.4647
154	1.6145	259	1.4466
158	1.5914	262	1.4387
162	1.5959	265	1.4314
166	1.5777	267	1.4242
170	1.6052	270	1.4205
173	1.6052	273	1.4205

Table XVII : Reflectivity of Silver = 6,800 A

T°K	Reflectivity	T°K	Reflectivity
40	1.6387	184	1.5300
70	1.6317	187	1.5174
75	1.6246	190	1.5052
81	1.6317	193	1.5021
86	1.6381	197	1.4961
91	1.6381	200	1.4901
97	1.6381	203	1.4752
101	1.6381	206	1.4694
107	1.6491	210	1.4665
112	1.6455	213	1.4608
117	1.6491	216	1.4812
122	1.6455	222	1.5113
126	1.6381	225	1.5301
130	1.6491	228	1.5331
134	1.6455	231	1.5557
138	1.6381	234	1.5524
143	1.6381	237	1.5589
147	1.6381	239	1.5557
150	1.6381	242	1.5524
154	1.6309	245	1.5589
158	1.6273	248	1.5689
162	1.6238	251	1.5855
166	1.6168	254	1.5959
170	1.5993	265	1.6131
173	1.5722	267	1.5924
177	1.5557	270	1.5924
181	1.5491	273	1.5689

Table XVIII : Reflectivity of Silver λ = 9,300 A

T°K	Reflectivity	T°K	Reflectivity
36	1.6193	190	1.6329
46	1.7105	193	1.6541
58	1.6818	197	1.6498
65	1.6700	200	1.6541
70	1.6770	203	1.6586
91	1.6850	206	1.6674
97	1.6894	210	1.6760
101	1.6894	213	1.6760
107	1.6805	216	1.6760
112	1.6674	219	1.6717
117	1.6629	222	1.6717
122	1.6674	225	1.6717
126	1.6629	228	1.6674
130	1.6629	231	1.6674
134	1.6586	234	1.6674
138	1.6541	237	1.6674
143	1.6586	239	1.6674
147	1.6541	242	1.6629
150	1.6457	245	1.6629
158	1.6287	248	1.6586
162	1.6287	251	1.6629
166	1.6329	256	1.6586
170	1.6244	262	1.6586
173	1.6161	265	1.6586
177	1.6122	267	1.6586
181	1.6244	270	1.6541
187	1.6329	273	1.6586

Table XIX : Reflectivity of Aluminium T = 290°A

λ A	Reflectivity
4,700	1.0000
5,225	1.0211
5,900	1.0604
6,500	1.1332
9,300	1.1980

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